


In presenting the dissertation as a partial fulfillment of the requirements for an advanced degree from the Georgia Institute of Technology, I agree that the Library of the Institute shall make it available for inspection and circulation in accordance with its regulations governing materials of this type. I agree that permission to copy from, or to publish from, this dissertation may be granted by the professor under whose direction it was written, or, in his absence, by the Dean of the Graduate Division when such copying or publication is solely for scholarly purposes and does not involve potential financial gain. It is understood that any copying from, or publication of, this dissertation which involves potential financial gain will not be allowed without written permission.



3/17/65
b

THE PHYSICAL ADSORPTION OF BENZENE ON BORON NITRIDE AND GRAPHITE

A THESIS

Presented to

The Faculty of the Graduate Division

by

Robert Earl Smallwood

In Partial Fulfillment

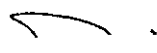
of the Requirements for the Degree


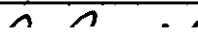
Master of Science in Chemistry


Georgia Institute of Technology

June, 1967

THE PHYSICAL ADSORPTION OF BENZENE ON BORON NITRIDE AND GRAPHITE

Approved; 


Chairman 


Date approved by Chairman: 18 May 1967

ACKNOWLEDGMENTS

I wish to thank Dr. Robert A. Pierotti, my research adviser, for his friendship, advice, and encouragement during my years of graduate study at the Georgia Institute of Technology.

Ensign Alvin C. Levy deserves special credit for preparation of the computer programs used in numerous calculations.

The aid that Mr. William Davis gave me, in analyzing benzene by chromatographic techniques, is greatly appreciated.

The advice and assistance given to me by Mr. Donald E. Lillie and Mr. James J. McAlpin was of immeasurable value towards the completion of this work.

This work was made possible by a research grant from the Petroleum Research Fund of the American Chemical Society. This support is gratefully acknowledged.

TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	ii
LIST OF TABLES.	iv
LIST OF ILLUSTRATIONS	v
SUMMARY	vi
Chapter	
I. INTRODUCTION	1
II. INSTRUMENTATION, EQUIPMENT, AND PROCEDURE.	3
III. COMPUTATIONS AND RESULTS	15
IV. CONCLUSIONS.	60
V. RECOMMENDATIONS.	63
LITERATURE CITED.	65

LIST OF TABLES

Table		Page
1.	BET Surface Areas in m^2/gram of Adsorbent.	28
2.	Benzene on Graphite at 273.16°K	29
3.	Benzene on Graphite at 288.16°K	31
4.	Benzene on Graphite at 298.16°K	33
5.	Benzene on Graphite at 303.16°K	35
6.	Benzene on Graphite at 323.16°K	37
7.	Benzene on Boron Nitride at 273.16°K	39
8.	Benzene on Boron Nitride at 288.16°K	42
9.	Benzene on Boron Nitride at 298.16°K	45
10.	Benzene on Boron Nitride at 303.16°K	48
11.	Isosteric Heats of Benzene on Graphite at 298.16°K	51
12.	Isosteric Heats of Benzene on Boron Nitride at 298.16°K	53
13.	ΔC_p^{ads} , ΔH^{ads} , ΔG^{ads} , and ΔS^{ads} of Benzene on Graphite at 298.16°K	55
14.	ΔC_p^{ads} , ΔH^{ads} , ΔG^{ads} , and ΔS^{ads} of Benzene on Boron Nitride at 298.16°K	57
15.	Limits on ΔC_p^{st} and ΔH^{st} for Both Adsorbents as a Function of the Weight Adsorbed	59

LIST OF ILLUSTRATIONS

Figure		Page
1.	Balance and Temperature Controller	5
2.	Pressure Measuring System.	6
3.	a. Benzene Reservoir System	
	b. Pumping System	9
4.	Isotherms for the Adsorption of Benzene on Graphite in the Low Pressure Region	19
5.	Isotherms for the Adsorption of Benzene on Graphite in the Intermediate Pressure Region.	20
6.	Isotherms for the Adsorption of Benzene on Graphite in the High Pressure Region.	21
7.	Isotherms for the Adsorption of Benzene on Boron Nitride in the Low Pressure Region	22
8.	Isotherms for the Adsorption of Benzene on Boron Nitride in the Intermediate Pressure Region.	23
9.	Isotherms for the Adsorption of Benzene on Boron Nitride in the High Pressure Region.	24
10.	Isosteric Heats of Adsorption as a Function of the Fractional Surface Coverage.	25
11.	Molar Integral Heats of Adsorption as a Function of the Weight of Benzene Adsorbed.	26
12.	Molar Integral Entropies of Adsorption as a Func- tion of the Weight of Benzene Adsorbed	27

SUMMARY

Only in the last few years have materials become available which have nearly homotattic surfaces. Considerable work on several graphitized thermal blacks has been done and some indications that boron nitride samples can also possess homotattic surfaces has been indicated. Due to the very great similarity between the two materials, it therefore follows that a study of the two adsorbents with a common adsorbate would be useful in theoretical considerations about physical adsorption.

The physical adsorption of benzene was measured on nearly homotattic samples of graphite and boron nitride by a vacuum balance-capacitance manometer system. For both adsorbents, Type II isotherms were obtained in the temperature range of 0-50°C.

Calculations of the isosteric heats of adsorption, the molar integral change of enthalpy and the integral change in entropy on adsorption showed that the two adsorbents are very similar when benzene is the adsorbate. Benzene was found to be more strongly adsorbed on graphite.

The benzene molecule on a graphite surface is hindered in its available rotational states at all coverages, while on a boron nitride surface, considerably more rotational freedom exists at low coverages.

A major difference between the two adsorbents exists when water is adsorbed on each material. Boron nitride chemisorbs water while, on graphite, adsorption is very small except at high relative pressures.

CHAPTER I

INTRODUCTION

While the phenomenon of physical adsorption on solids has been known and studied for many years, only recently has this phenomenon been studied on homotattic surfaces. On a solid with a heterogeneous surface, various energy sites exist with respect to adsorbate - adsorbent interaction. The effects of these different energy sites make it difficult to systematically study adsorbate - adsorbent interactions as these interactions have only a small effect compared to the large interactions of localized adsorption on the higher energy sites or "hot spots."

In the case of a homotattic solid, only one energetic site is accessible to the adsorbate, neglecting of course the very small relative number of solid state defect sites and edge sites. The graphitization of various carbon blacks by heating in the absence of air to about 3000°C results in a solid surface that is almost entirely composed of one type of energy site. The graphite crystals thus produced are primarily doubly truncated hexagonal and octagonal bipyramids with the surface almost entirely of the graphite basal plane.^{1,8}

Boron nitride is like graphite in that it possesses a hexagonal-layer-lattice structure. It is also isoelectronic and isometric with graphite. While graphite is an electrical conductor, boron nitride is not. For these reasons, a comparison of the two is of considerable interest. As in the case of graphitized carbon blacks, different samples

of boron nitride have the same adsorption potential even if they have apparently different surface areas. Thus, properly prepared boron nitride samples should show similar interaction energies with an adsorbent.⁷

Benzene is a planar non-polar molecule containing delocalized π -electrons. The carbon - carbon bond in benzene is about the same length as the carbon - carbon bond in graphite and the boron-nitrogen bond in boron nitride. When benzene is adsorbed on a non-polar surface, the dispersion attraction is balanced by electrostatic repulsions. Due to the π -electrons, benzene adsorption is greatly influenced by the presence of hydroxyl groups on a solid surface.¹

The purpose of this study is to compare the two adsorbents as far as benzene adsorption is concerned. A gravimetric method of obtaining complete isotherms was used. The primary purpose of this paper is to present the necessary experimental data so that more advanced theoretical treatments of solid-gas adsorption will result.

CHAPTER II

INSTRUMENTATION, EQUIPMENT, AND PROCEDURE

In any study of the adsorption of a gas on a solid surface, the fundamental data to be obtained are the amounts of gas adsorbed at given temperatures and pressures. Various methods have been devised, but only two, a measurement of the pressure drop in a system upon adsorption and/or a method to measure the increase in weight of the solid due to adsorbed gas (or gasses), are practical for powders.^{5,6,7}

In this study, it was necessary to use the gravimetric method due to the physical properties of benzene vapor. The condensation of benzene in a McLeod gauge while measurements were being made and the high solubilities of benzene in stopcock grease made accurate measurements of the decrease in pressure in a system difficult if not impossible.

The first apparatus used a modified McBain balance. A beryllium copper spring, kindly donated by the Instrument Specialities Company, Inc. of Little Falls, N. J., was used. This spring had a deflection of 0.166 mm/mg, constant throughout the range 0-1000 mg. A M-301 cathetometer manufactured by the Gaertner Scientific Corp. was used to measure the deflection of the spring as adsorption occurred. With the cathetometer, the readings of ± 0.001 mm could be made. Using the cathetometer with the beryllium copper spring, a theoretical accuracy of approximately ± 0.0002 mg per reading could be obtained. However, due to vibrations inherent in the apparatus, readings on the order of ± 0.1 mg per reading were the best

that were obtained. For this reason, the McBain balance was discarded in favor of a Cahn Microbalance.

The Cahn RG Automatic Electrobalance (Cahn Instrument Company, Paramount, Calif.) was placed into the system (Figure 1) inside a No. 2005 Cahn glass vacuum bottle. Readings of weight changes were at first obtained with a null-meter, but more satisfactory results were obtained through the use of a Graphicorder-10 No. 8035 purchased from Dynatronic Instrument Corp., Melrose Park, Illinois. Only one mass range of the balance was used, the 0-10 mg mass range. In connection with the recorder, a measurement of a ± 0.001 mg change could be made with the Cahn balance throughout the entire 0-10 mg mass range. However, due to noise in the recorder and occasional zero shifts in both the balance and recorder as well as the inherent error of 0.05 percent in the mass dial readings, the absolute accuracy was only ± 0.005 mg per reading.

The balance controls were set as follows: Mass Dial Range - 10 mg, Recorder Range - 0.4 mg, Factor - 1, and Filter - 3. The recorder was used entirely on its one millivolt range. Both the balance and recorder were calibrated according to the method in the Cahn Instrument Manual. The sample was placed in thin wall glass buckets, which were suspended from 0.002 inch nichrome wire. The samples were covered with a layer of Pyrex glass wool. The total weight of the bucket and its component was about 0.9 gram made up of about 0.5 g of sample, 0.3 g bucket weight, and 0.1 g of glass wool.¹¹

After the failure of attempts to measure pressure directly with a mercury manometer, a capacitance manometer was used in connection with a McLeod gauge and a mercury manometer (Figure 2). A mercury manometer was

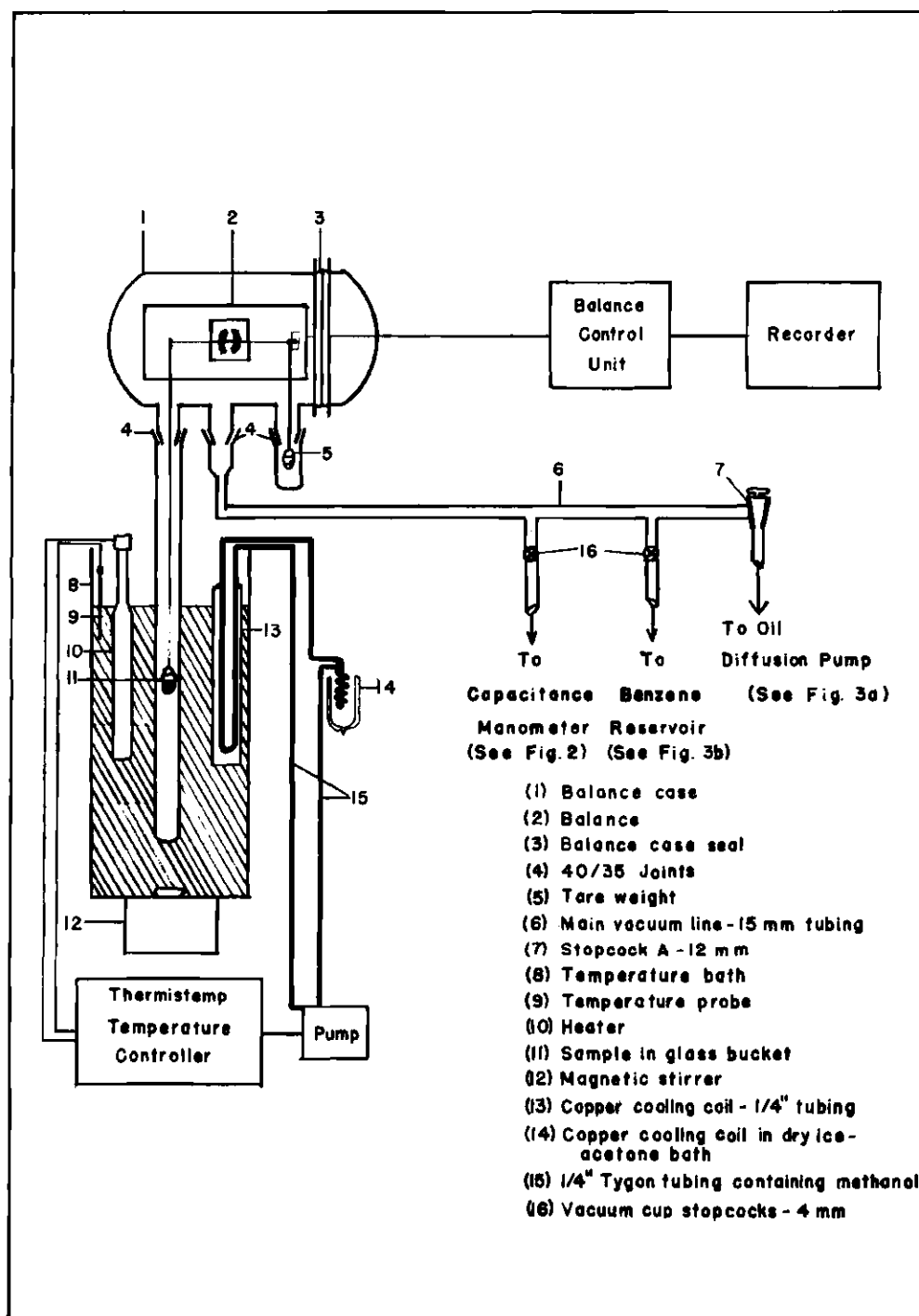


Figure 1. Balance and Temperature Controller

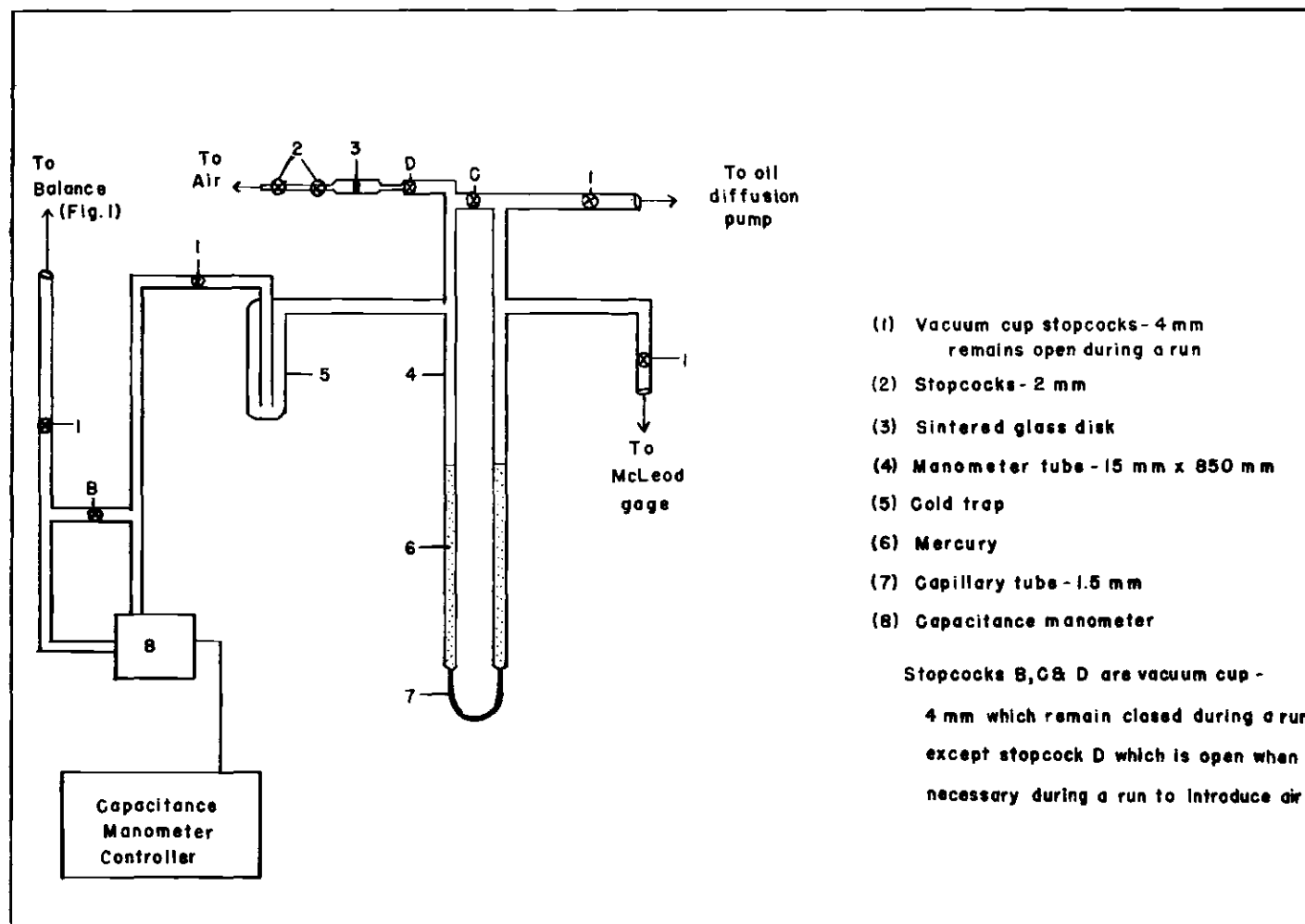


Figure 2. Pressure Measuring System

unsuccessful due to mercury contamination of gold plated parts on the balance and the large relative error in the pressure measurements associated with the manometer at low pressures. A Granville-Phillips capacitance manometer Series 212 Model B was used as a direct reading instrument. The capacitance manometer was used only on the one unit range as calibration and zero settings changed between the 0.1 range and the one and ten unit ranges. The capacitance reading was checked against the McLeod gauge and the sensitivity of the capacitance manometer was adjusted until a reading corresponding to the measured pressure was obtained. The manufacturer's rated sensitivity of the capacitance manometer was 5×10^{-3} Torr (or 5×10^{-3} mm of Hg), but using the one unit range, a sensitivity of better than 2×10^{-3} Torr was reproducibly obtained.

The McLeod gauge used had three ranges: 0-0.3 Torr, 0-1.50 Torr, and 0-9.60 Torr with errors of $\pm 10^{-3}$ Torr, $\pm 5 \times 10^{-3}$ Torr, and $\pm 10^{-2}$ Torr, respectively. The mercury level in the manometer was measured by means of a Gaertner M-911 cathetometer. In each McLeod gauge range, an accuracy of 0.2 percent was obtained. In combination with the capacitance manometer, an error of less than one percent in absolute pressure measured throughout the range 0-10.6 Torr could be realized. The error was thus ± 0.002 Torr, at pressures under 0.100 Torr. Thus, in this case, the error was much greater than the one percent at higher pressures obtained due to difficulty in leveling the mercury levels.⁵

The mercury manometer consisted of a 16 mm U-tube, filled by distillation under vacuum of less than 1×10^{-3} with mercury previously washed with nitric acid. The manometer was used to measure pressures above 9.60 Torr. The manometer was read with a M-911 cathetometer to an

absolute accuracy of ± 0.10 Torr. The manometer, as the McLeod gauge, was, of course, used in connection with the capacitance manometer.

The entire system was evacuated to a pressure of less than 1×10^{-5} Torr through the use of a Welch Duo-Seal No. 1400 vacuum pump in series with a Consolidated Vacuum Corp. VMF No. 11 air-cooled oil diffusion pump. A cold trap using dry ice-acetone mixture was placed at all times between the capacitance manometer and the mercury containing McLeod gauge and manometer (Figure 3b).

All stopcocks were vacuum-cup 4 mm Corning No. 7544 except the main vacuum line stopcock A (Figure 1), which was a 12 mm Corning No. 7548. Apiezon T grease was used on all stopcocks except the 12 mm stopcock where Apiezon N was employed.

The balance case presented the most difficulty. It was only successfully sealed by a combination of Apiezon T grease and Apiezon W wax. The balance case was connected to the rest of the system with 40/35 joints greased with Apiezon T grease.

An excellent check for leaks was to attempt to condense the benzene out of the system with a dry ice-acetone bath after the completion of a run; if condensation was rapid (50 Torr to 0.1 Torr in about 10 minutes), there was no measurable quantity of air that had leaked into the system. However, if a leak had occurred, then condensation was very slow--10 to 20 times slower for the same pressure drop than if no leak had occurred. This method could detect about 0.005 Torr pressure of air in the system.

A 40 mm OD \times 40 cm Vycor tube was wrapped with nichrome wire and covered with wet asbestos sheet and then baked. This furnace was placed

Fig. 3a Benzene Reservoir System

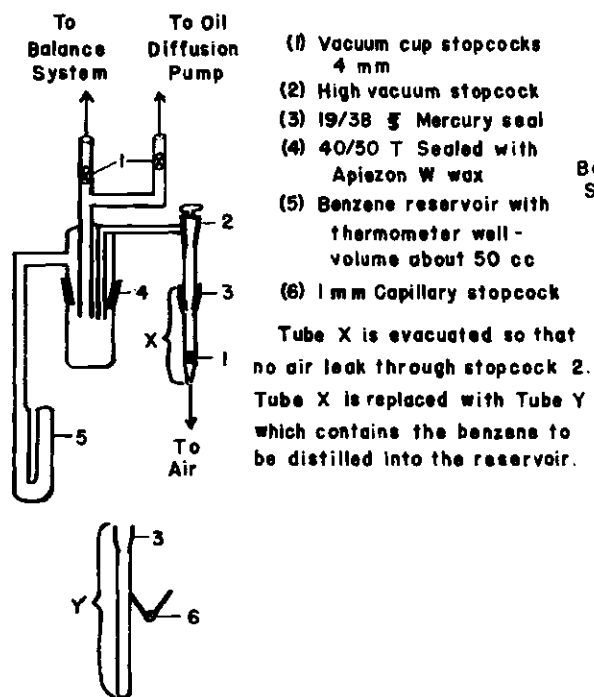


Fig. 3b Pumping System

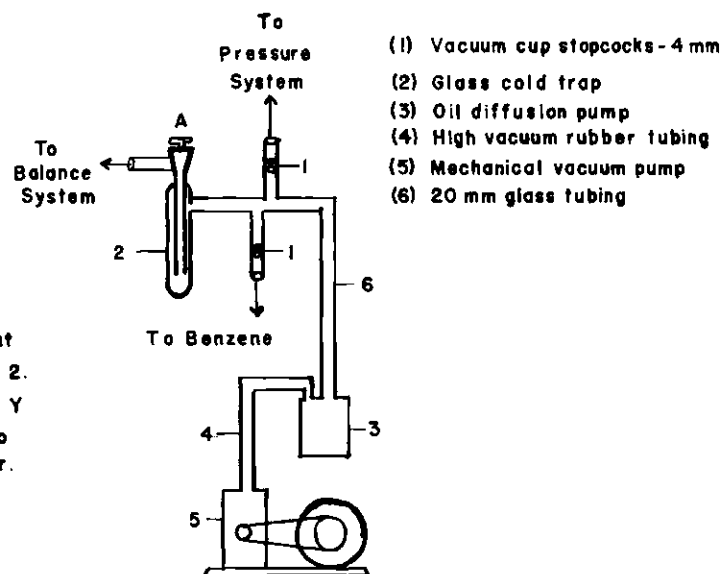


Figure 3.

around the sample which was under a high vacuum and the sample heated to $510^{\circ}\text{C} \pm 20^{\circ}\text{C}$, usually overnight although sometimes longer. Graphite was easily outgassed by this method. A new sample of graphite lost about three mg per gram of sample upon the above treatment. A reproducible run could be made after one heating after exposure to air.

A sample of boron nitride previously exposed to air was much more difficult to outgas. A fresh sample lost around 15 mg per gram of sample after a day's heating at $525^{\circ}\text{C} \pm 25^{\circ}\text{C}$ and about one mg per gram after further heating for two days under the same conditions before reproducible results could be obtained. Even a very small quantity of air leakage was enough to necessitate the above treatment. Boron nitride, like graphite, could be outgassed overnight after exposure to benzene if heated to $510^{\circ}\text{C} \pm 20^{\circ}\text{C}$. The surface remains the same after exposure to air and proper outgassing, but until this was recognized, erroneous results were obtained.

Two different methods were used to control temperature in the adsorbent temperature bath. For the isotherms run at 0.00°C and -20.8°C , slush baths of distilled water and ice and liquid and solid dimethyl succinate (Eastman No. 127), respectively, were used. The dimethyl succinate bath was not very satisfactory due to condensation of water from the air and also lack of homogeneity of temperature in the bath. For this reason, only the benzene on graphite was studied with this bath. The ice-water bath never varied over $\pm 0.02^{\circ}\text{C}$. The slush baths were maintained in a Dewar flask.

The second method consisted of a system utilizing a Thermistemp temperature controller, Model 71, a magnetic stirrer, a heater, a cooling

system and a 100 mm \times 50 cm Pyrex beaker. The Thermistemp controller is stated by the manufacturer, Yellow Springs Instrument Co., to be able to regulate temperature to $\pm 0.05^\circ\text{C}$, and this control was at all times obtained. The stirrer remained on all of the time. The heater wattage was regulated by a powerstat and an on-off controller. The cooling system, also activated by the controller, consisted of a fluid pump, a copper coil placed in a cold bath, and a copper coil placed into the adsorbent temperature bath. The cooling fluid was methyl alcohol. The cooling system was not used in the 30°C and 50°C baths as loss of heat to the room was all that was necessary to cool the bath. The cold bath consisted of ice for the 25°C isotherm and dry ice-acetone for the 15°C isotherm bath. The temperature of the various baths was read with thermometers calibrated against a platinum resistance thermometer.

The reagent grade benzene (Baker thiophene free) used in these studies was distilled into the benzene container under a vacuum of about 1×10^{-2} Torr (Figure 3b). The benzene was distilled between the two tubes (Figure 3a) of the benzene container under a vacuum of 5×10^{-4} Torr by placing a dry ice-acetone bath around one tube and maintaining the other tube at room temperature. This was repeated at least three times, in each distillation, the first distillation portion and the residue were removed by pumping for several minutes while the other tube was maintained at -78°C by a dry ice-acetone bath. Gas chromatography measurements indicate that the benzene consists of less than 0.02 percent of foreign material--probably toluene.

A typical isotherm run usually took over six hours. The sample was heated overnight to about 520°C . The tubular furnace was then re-

moved and the temperature bath then placed around the sample tube. The sample remained under vacuum that was at least as low as 1×10^{-5} Torr. All stopcocks were turned so that any gas absorbed in the grease could escape and was pumped out while the sample was still being heated. Stopcocks A, B, and C were closed (Figures 1 and 2); this, of course, isolated the sample from the rest of the system as well as the mercury pressure measuring devices from the rest of the system. A small quantity of air was introduced through the air inlet (Figure 2) to calibrate the capacitance manometer. The pressure of air introduced was on the order of 0.4 Torr and was measured with the McLeod gauge, the capacitance manometer control being adjusted accordingly. The zero point weight of the sample was noted and a small quantity of benzene was then allowed into the sample system while the benzene tube was in a cold bath, usually at -60°C to start. After adsorption had occurred and no further change was noted in sample weight, another dose of benzene was added, and so on. The temperature bath surrounding the benzene tube was allowed to warm up so that the temperature was such that the pressure in the benzene container was never much higher than in the sample part of the system. This procedure was continued until the pressure in the sample system reached about 80 Torr or the weight increased out of the range of the balance. The capacitance manometer was, of course, varied by additional doses of air, each measured by the appropriate measuring device. At each dosage of benzene, the weight increase and the pressure were measured and noted. After an isotherm was completed, the benzene was removed from the system by placing the benzene-containing tube in a dry ice-methyl alcohol bath and allowing the vapor to condense until a pressure of about 0.050 Torr was

obtained. While desorption occurred, the air pressure was also reduced to allow the capacitance gauge to always remain in range. To determine desorption isotherms, several pressure decreases were carried out, each decrease in pressure in the system resulting in one point on the desorption curve after equilibrium was obtained. The sample system pressure was further decreased and another desorption point obtained. The pressure was decreased until no further decrease occurred, then the sample system was opened to the pumping system to further reduce the pressure. A pressure of only about 0.002 Torr could be obtained by this method in a reasonable time, as degassing stopcock grease of benzene was slow. The entire system was then opened to the pumps and the temperature bath removed and the tubular furnace placed around the sample tube and brought up to $510^{\circ}\text{C} \pm 20^{\circ}\text{C}$. The sample was then heated overnight and another isotherm was obtained the next day.

The graphite used in this work was obtained from Dr. Carl Prenzl. It was prepared by Dr. W. Smith of Godfrey Cabot Company and designated Sterling FT (2700°C). It is apparently the same as the graphite designated P-33 (2700°C).

Boron nitride powder, 325 mesh, was obtained from the Carborundum Company. Spectrographic analysis showed this sample to be greater than 99.92 percent pure. X-ray diffraction showed it to be highly crystalline, having a crystal structure very similar to that of graphite. This sample came from the same lot as the sample used by Pierotti for other studies.

The vapor pressure (P) of benzene at a temperature (T) was calculated from the Antoine equation¹³

$$\log_{10} P_O = A - \frac{B}{C + t}$$

where $A = 9.1064$ for solid benzene and 6.90565 for liquid benzene

$B = 1885.9$ for solid benzene and 1211.033 for liquid benzene

$C = 244.2$ for solid benzene and 220.790 for liquid benzene

$t =$ temperature in degrees Centigrade

CHAPTER III

COMPUTATIONS AND RESULTS

The pressure and corresponding weight change were plotted on 50×150 cm graph paper, divided into 1×1 mm squares. Three graphs were used for each isotherm: (1) for pressures from zero to one Torr (one Torr pressure was equivalent to 20 cm along the abscissas); (2) for pressures from one to ten Torr (one Torr pressure was equivalent to five cm along the abscissas); and (3) for pressures from ten to one hundred Torr (one Torr pressure was equivalent to five mm along the abscissas). In all cases, ten centimeters along the ordinate was equivalent to one milligram in weight change per gram of sample. Thus, on these graphs, a point from the curve can be read to ± 0.01 mg per gram of sample. The pressure in turn can be determined for the 0-1 Torr, 1-10 Torr, and 10-100 Torr graphs to ± 0.0025 Torr, ± 0.01 Torr, and ± 0.05 Torr, respectively.

After all the data points for an isotherm were determined, a smooth curve was drawn as closely as possible to all of the experimental points. All values of weight versus pressure used in the pertinent calculations were obtained from the smooth curve so drawn. The graphs of the isotherms are shown in Figures 4 through 9. The various numerical values are presented in Tables 2 through 10.

The surface areas were obtained by use of the BET equation⁴

$$\frac{P}{v(P_0 - P)} = \frac{1}{v_m C} + \frac{C - 1}{v_m C} \frac{P}{P_0}$$

where P = pressure in Torrs at a given point

v = volume of gas adsorbed in cm^3 corrected to STP at a pressure P

P_0 = vapor pressure of adsorbate at the isotherm temperature

v_m = volume of gas adsorbed to form a monolayer in cm^3 at STP

C = a "constant" at a given temperature

The BET equation was used over the range of P/P_0 from 0.05 to 0.15.

The necessary experimental data were tabulated so that upon plotting on graph paper the values of v_m and C could be obtained (Table 1). The surface area was then determined by means of the equation

$$\Sigma = 0.269 \times v_m \times \sigma_0$$

where v_m = volume of monolayer adsorbed in cm^3 at STP

σ_0 = molecular cross section of adsorbate in \AA^2 (for benzene 40 \AA^2)

Σ = surface area in m^2 per gram of sample

The isosteric heats ΔH^{st} were calculated by a Clausius-Clapeyron type of expression for a given weight adsorbed (W_a)¹⁰

$$\ln P = - \frac{\Delta H^0}{RT} + \frac{\Delta C_p^{\text{st}}}{R} \ln T + C$$

where $\Delta H^{\text{st}} = - \Delta H^0 + \Delta C_p^{\text{st}}(T)$ at a given weight adsorbed (W_a) for each

$$\Delta H^{st}, \Delta C_p^{st}, \text{ and } \Delta H^O.$$

The values of ΔH^O , ΔC_p^{st} , and ΔH^{st} are to be found in Tables 11 and 12, and Figure 10 shows the graphs of ΔH^{st} versus weight adsorbed. The errors in the isosteric heats for the graphite system are approximately ± 800 cal/mole at $\theta = 0.1$; ± 300 cal/mole at $\theta = 0.25$; ± 175 cal/mole at $\theta = 0.4$; ± 125 cal/mole at $\theta = 0.5$; ± 75 cal/mole at $\theta = 0.7$; and ± 50 cal/mole at $\theta = 1.0$ and above. For the BN system, the errors are approximately ± 300 cal/mole at $\theta = 0.1$; ± 100 cal/mole at $\theta = 0.2$; and ± 50 cal/mole at $\theta = 0.1$ and above. Because of the computations involved in determining the equilibrium heats, it is difficult to assign uncertainties to the reported values, but we believe them to be approximately the same as the uncertainties in the isosteric heats.

The molar integral change of enthalpy of the system upon adsorption, ΔH^{ads} , was found by the same Clausius-Clapeyron expression as used to determine ΔH^{st} , except that instead of evaluating the enthalpy, at constant weight, it was evaluated at constant spreading pressure (Π was used). The equation

$$\Pi = \frac{RT}{22,400} \int_0^P v \, d \ln P$$

was programed so that the computer could integrate the area defined by the curve of volume adsorbed versus the pressure.¹⁰ Values of Π so obtained are to be found in Tables 2-10.

The integral molar Gibbs free energy is expressed by the equation

$$\Delta G^{ads} = RT \ln \frac{P}{760}$$

where 760 Torr pressure is the standard state of the gas. All values of ΔG^{ads} were calculated for 298.16° K using in all cases the value of P in Torr for the 298.16° K isotherms.¹⁰

The integral molar entropy of adsorption, ΔS^{ads} , was obtained from the expression

$$\Delta S^{\text{ads}} = \frac{\Delta H^{\text{ads}}}{T} - \frac{\Delta G^{\text{ads}}}{T}$$

The values at 298.16° K of ΔH^{ads} , ΔG^{ads} , ΔS^{ads} , and ΔC_p^{ads} are given in Tables 13 and 14. Figure 11 displays graphs of ΔH^{ads} versus W_a while ΔS^{ads} versus W_a is shown for each system in Figure 12. The errors associated with these thermodynamic values are shown in Table 15, calculated in the manner described by Hill.¹²

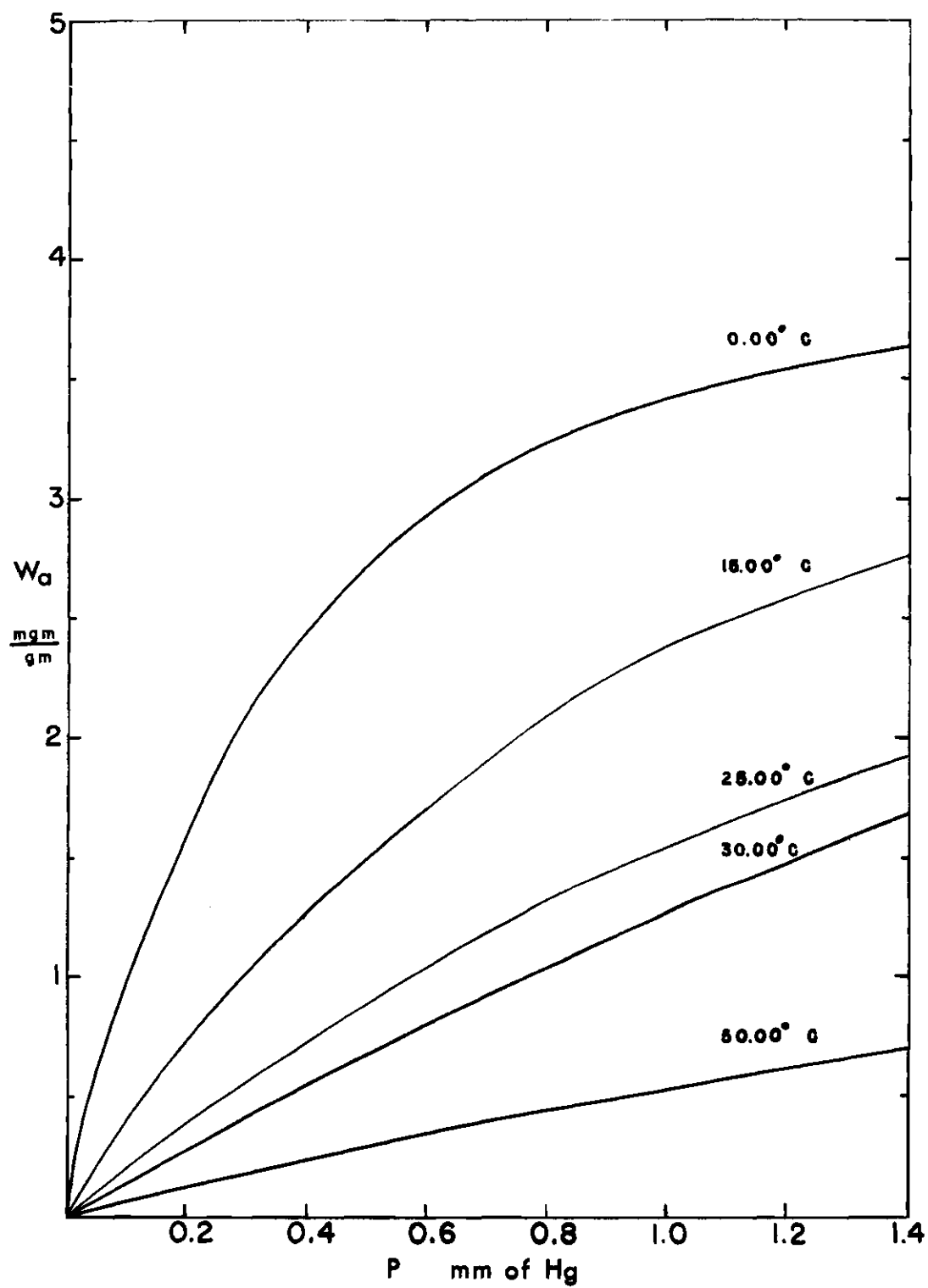


Figure 4. Isotherms for the Adsorption of Benzene on Graphite in the Low Pressure Region

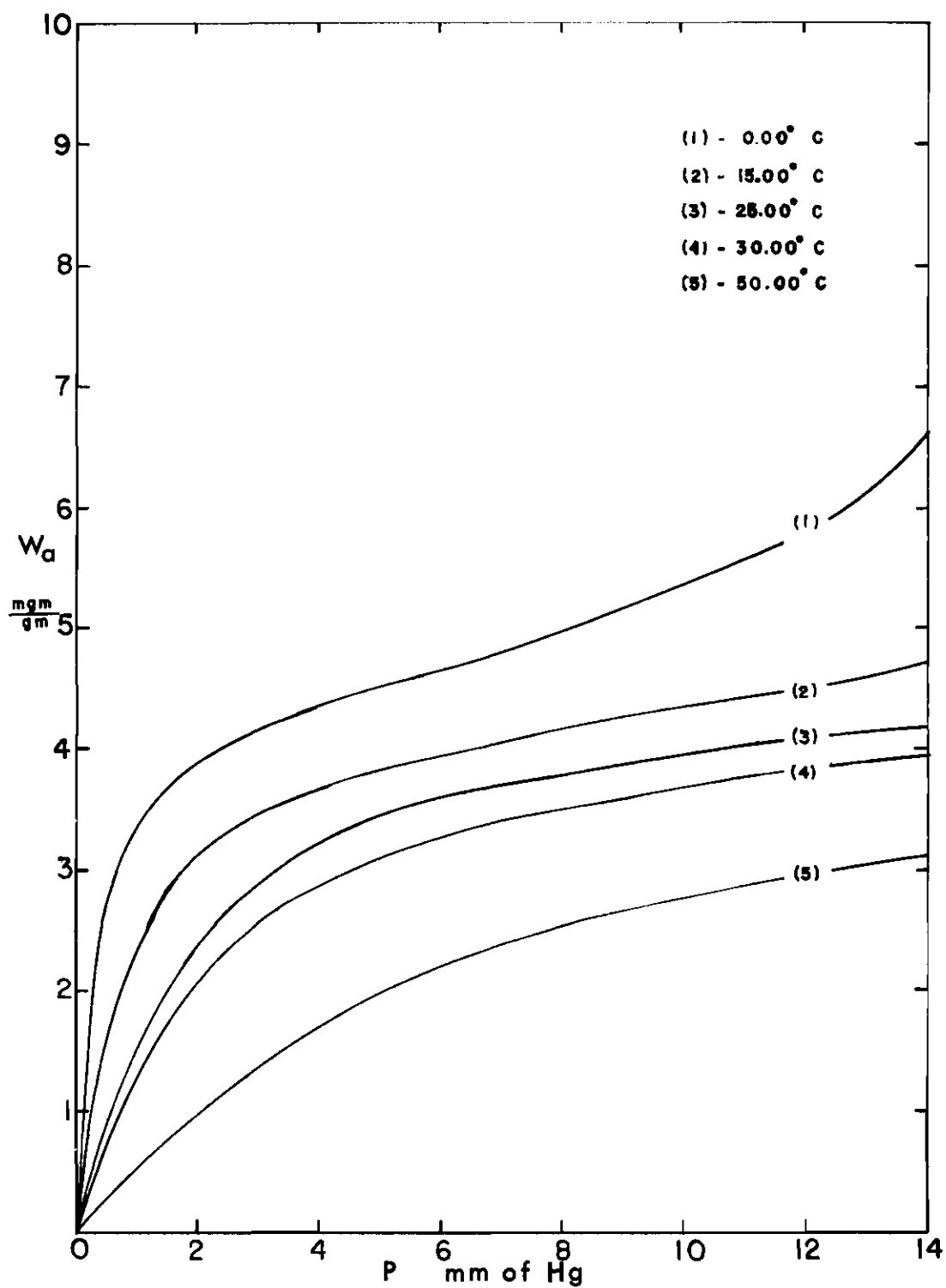


Figure 5. Isotherms for the Adsorption of Benzene on Graphite in the Intermediate Pressure Region

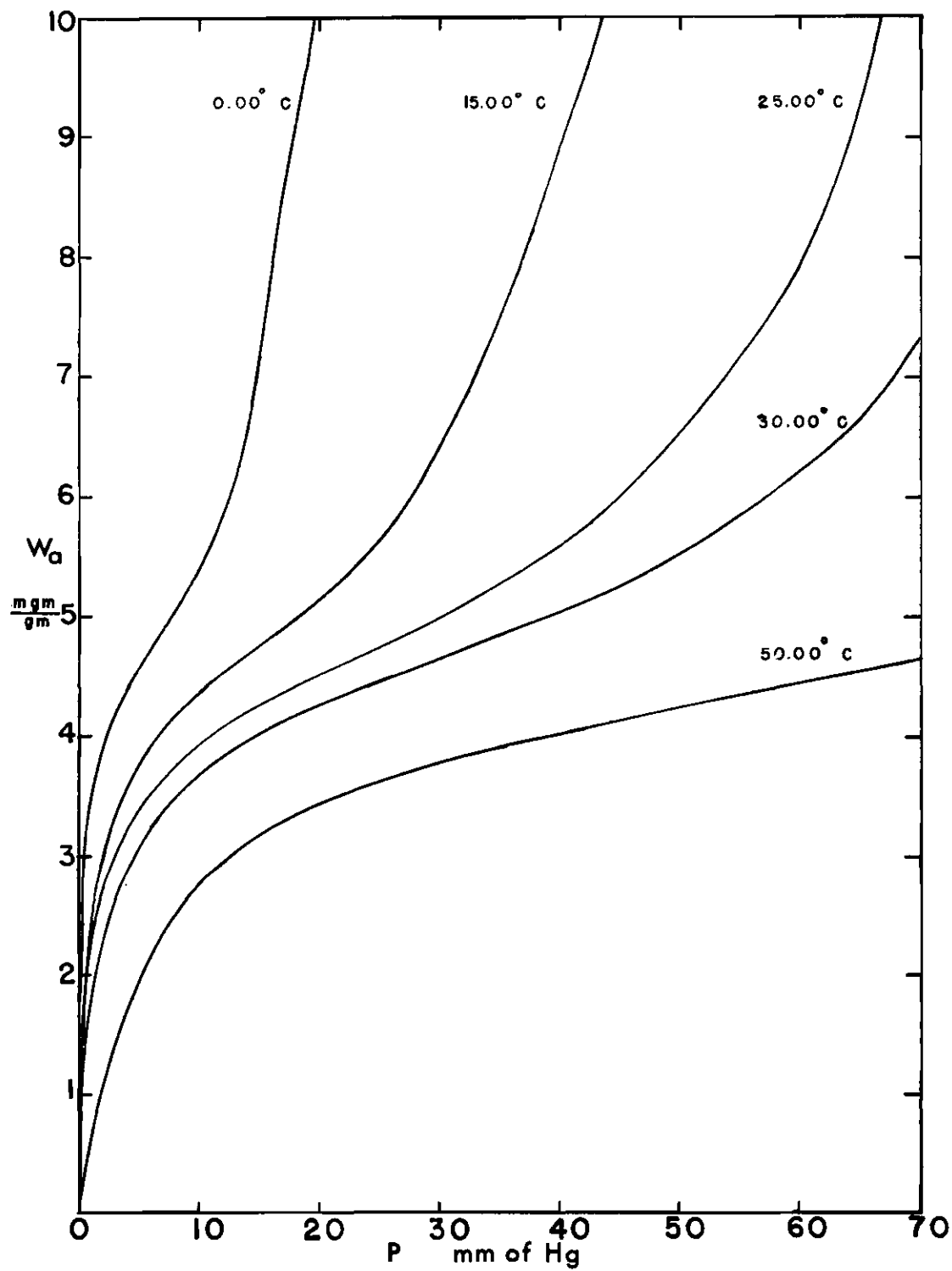


Figure 6. Isotherms for the Adsorption of Benzene on Graphite in the High Pressure Region

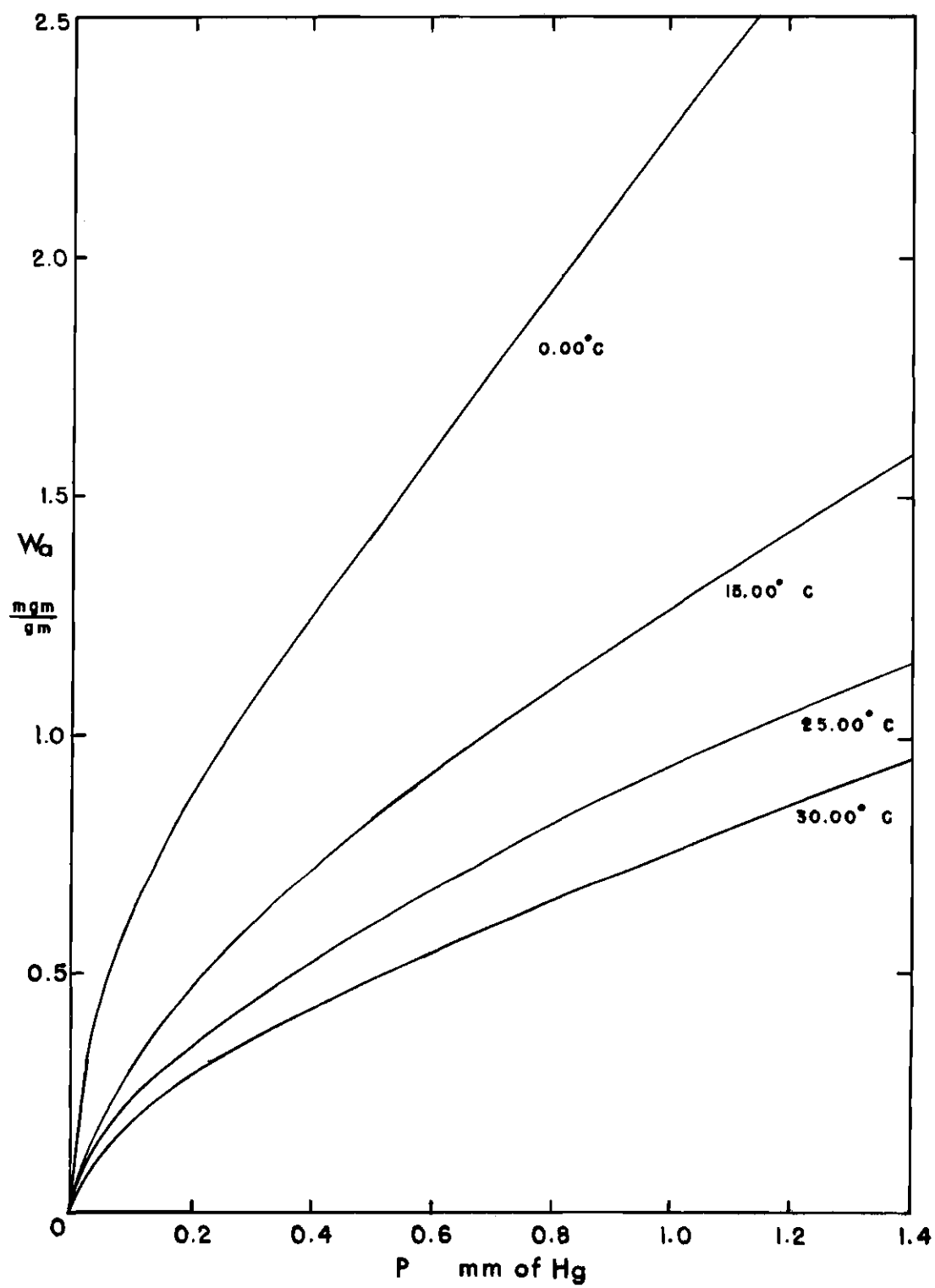


Figure 7. Isotherms for the Adsorption of Benzene on Boron Nitride in the Low Pressure Region

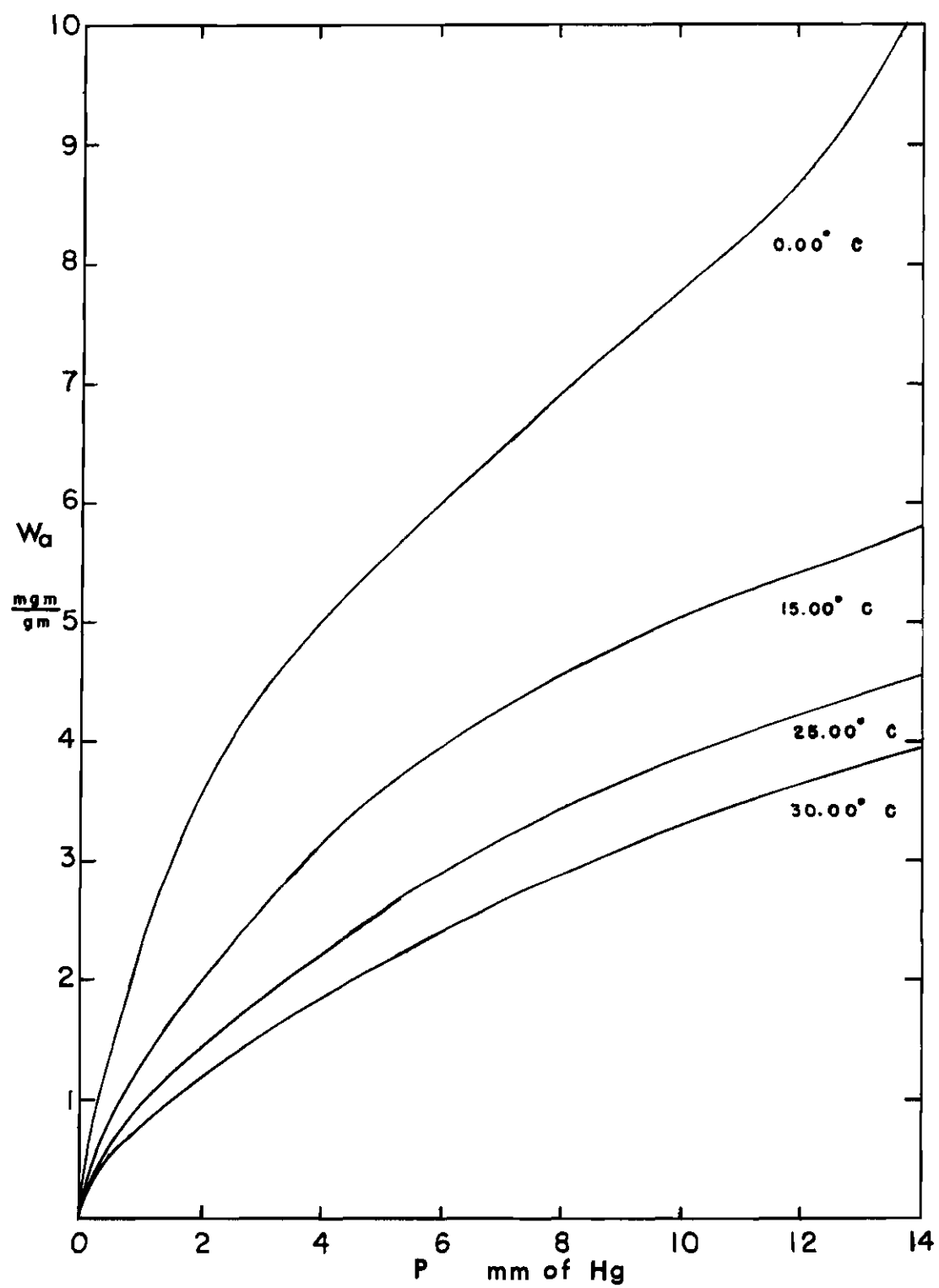


Figure 8. Isotherms for the Adsorption of Benzene on Boron Nitride in the Intermediate Region

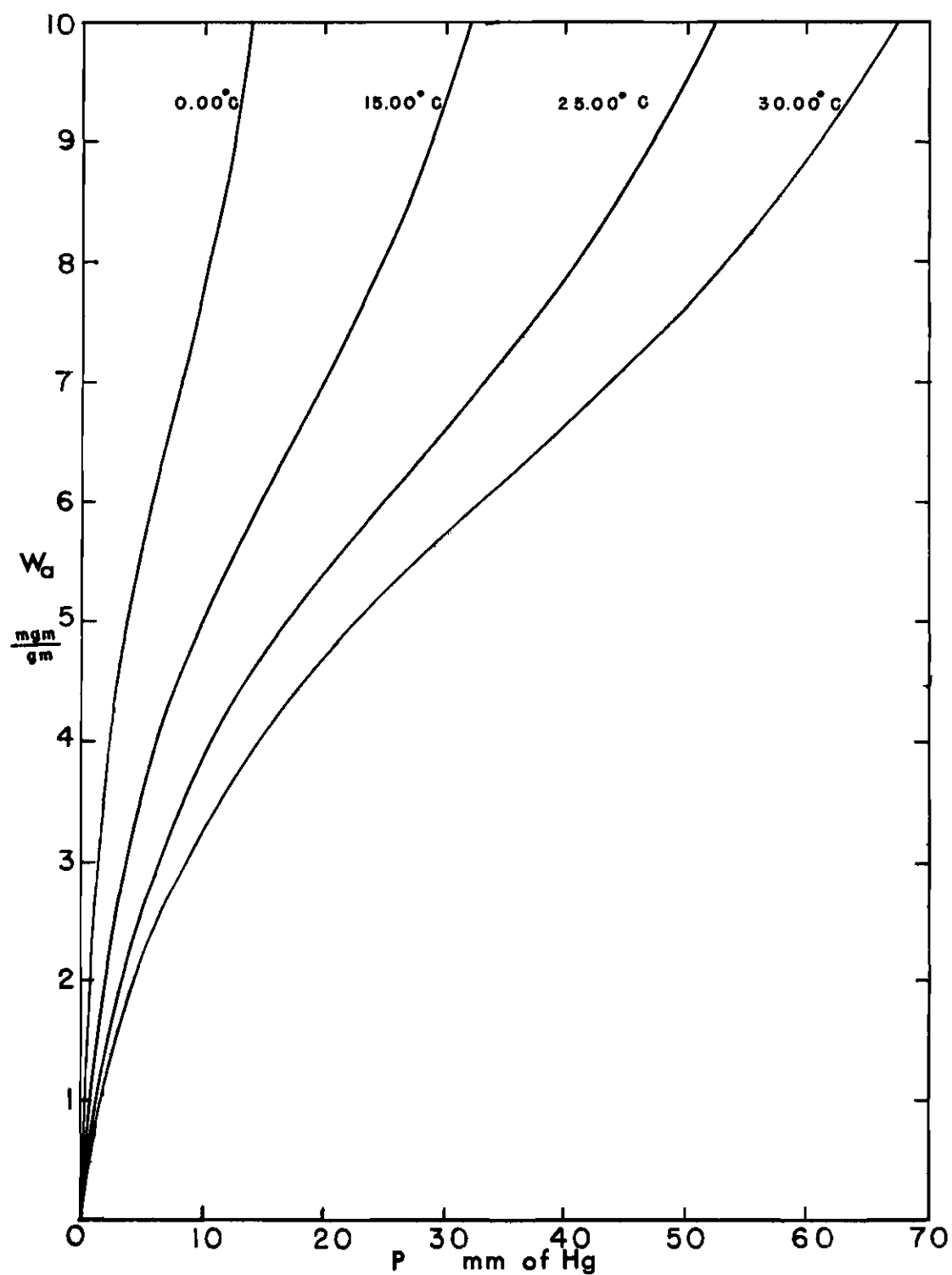


Figure 9. Isotherms for the Adsorption of Benzene on Boron Nitride in the High Pressure Region

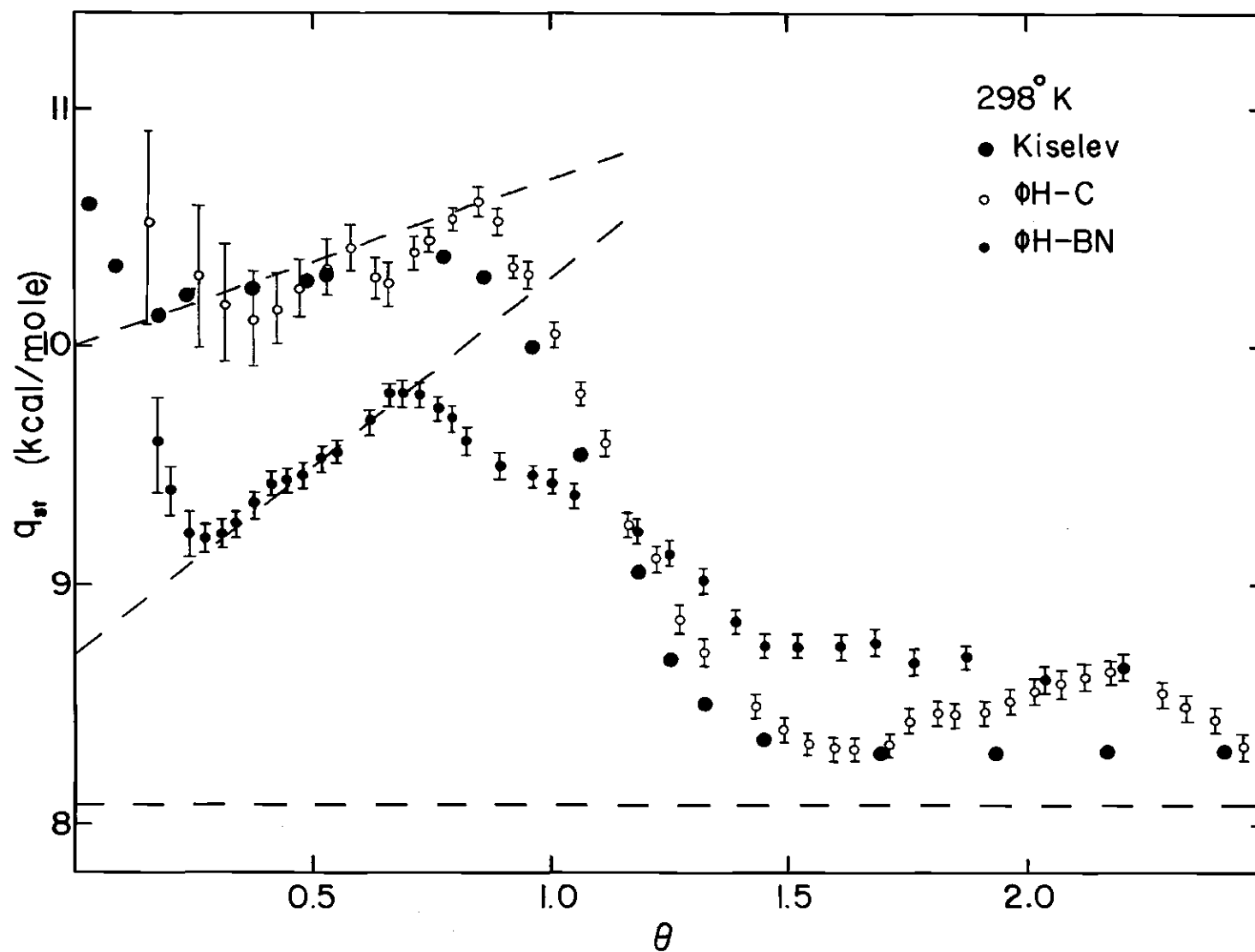


Figure 10. Isosteric Heats of Adsorption as a Function of the Fractional Surface Coverage

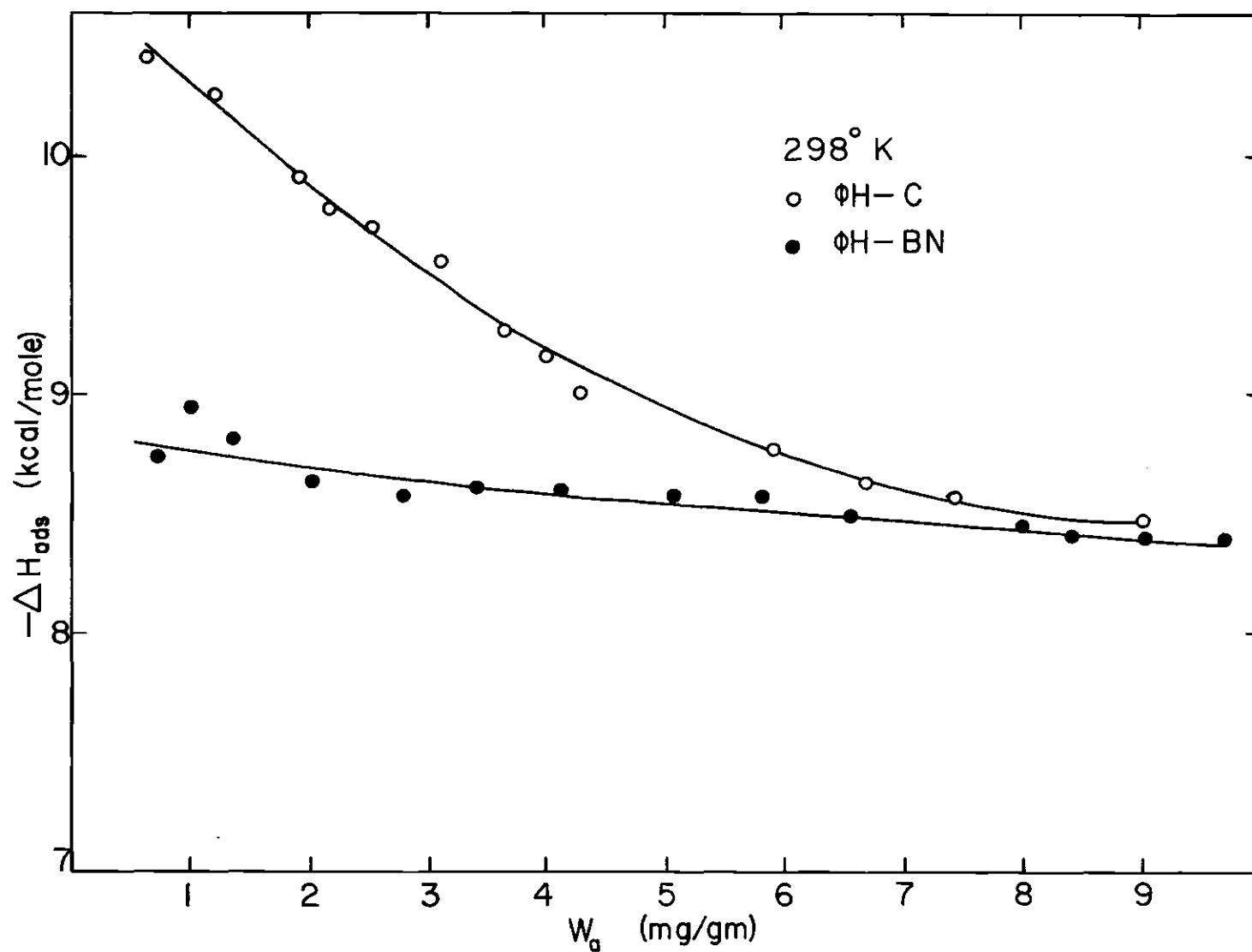


Figure 11. Molar Integral Heats of Adsorption as a Function of the Weight of Benzene Adsorbed

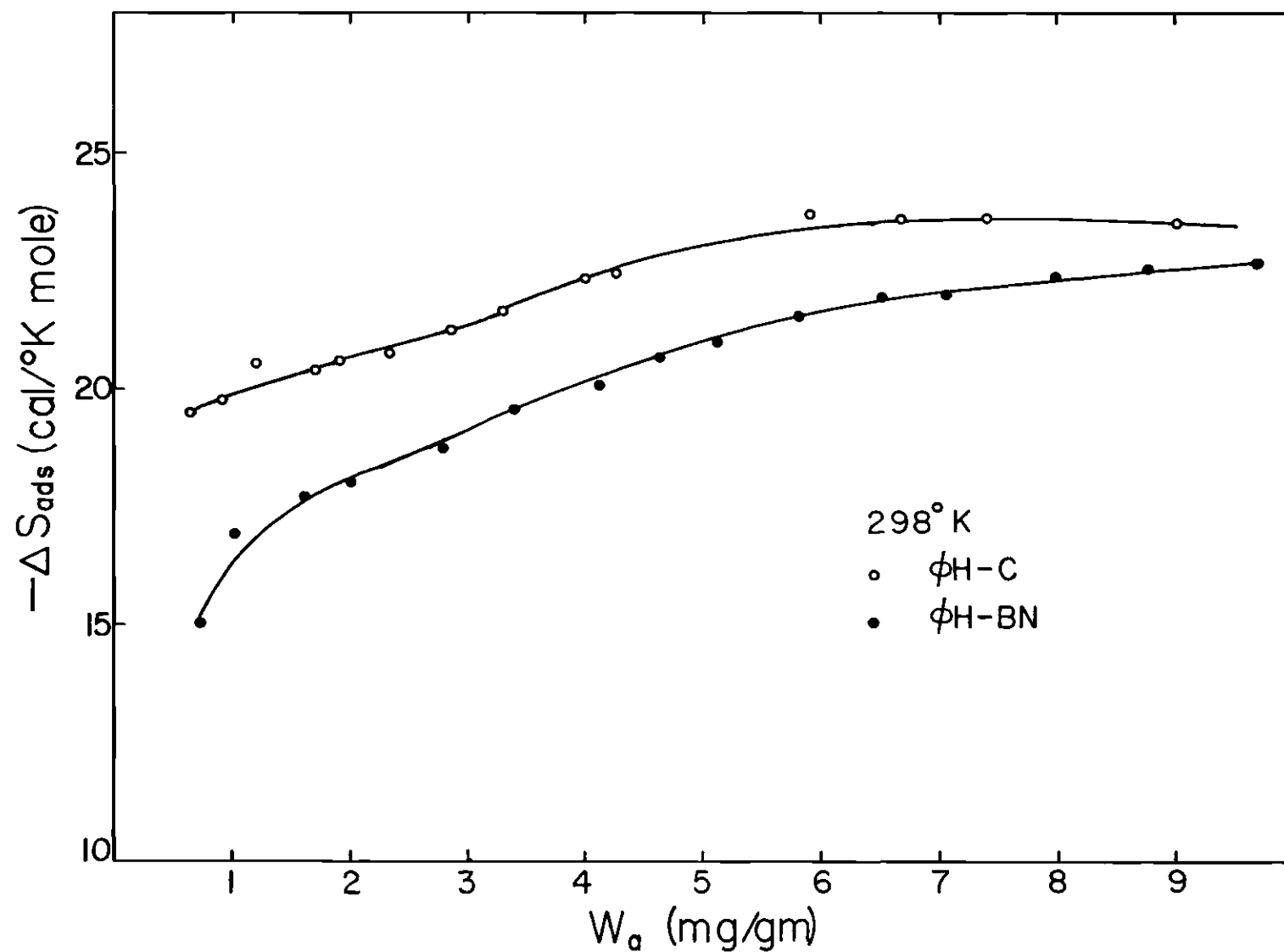


Figure 12. Molar Integral Entropies of Adsorption as a Function of the Weight of Benzene Adsorbed

Table 1. BET Surface Areas in m^2/gram of Adsorbent

T° K	Graphite	Boron Nitride
273.16	11.8	19.1
288.16	11.7	18.9
298.16	11.6	18.0
303.16	11.6	17.7
323.16	11.6	17.3
Average	11.7 ^a	18.3 ^b
W_m	3.77 mg/g of sample	5.93 mg/g of sample

^aThe area of this black has been estimated to be $10 \pm 2 \text{ m}^2/\text{g}$ by Halsey et al.¹⁴; Stepheight measurement of Ar yields 12.5^{15} ; BET areas using N_2 are about $12.2 \text{ m}^2/\text{g}$; Kiselev reports the BET area for FT (2800) as $12.2 \text{ m}^2/\text{g}$ using benzene.¹

^bThe BET v_m of this sample has been found to be quite temperature dependent for a number of gases including argon, nitrogen, and krypton. Areas from about 18 to $23 \text{ m}^2/\text{g}$ have been found depending upon the temperature.

Table 2. Benzene on Graphite at 273.16° K
 $P^0 = 24.19$ mm of Mercury

W_a mg/gm	P mm of Hg	$\frac{P}{P^0}$	Π dynes/cm
0.100	0.003	0.000124	0.11
0.200	0.008	0.000331	0.28
0.300	0.016	0.000661	0.55
0.400	0.027	0.00112	0.92
0.500	0.039	0.00161	1.30
0.600	0.052	0.00215	1.70
0.700	0.065	0.00269	2.09
0.800	0.080	0.00331	2.52
0.900	0.095	0.00393	2.93
1.000	0.110	0.00455	3.33
1.100	0.125	0.00517	3.71
1.200	0.140	0.00579	4.08
1.300	0.155	0.00641	4.43
1.400	0.170	0.00703	4.78
1.500	0.186	0.00769	5.14
1.600	0.202	0.00835	5.48
1.700	0.218	0.00901	5.82
1.800	0.236	0.00976	6.19
1.900	0.255	0.0105	6.57
2.000	0.275	0.0114	6.96
2.100	0.297	0.0123	7.38
2.200	0.320	0.0132	7.80
2.300	0.360	0.0143	8.52
2.400	0.388	0.0158	9.00
2.500	0.422	0.0172	9.57
2.600	0.456	0.0187	10.11
2.700	0.488	0.0202	10.61
2.800	0.528	0.0218	11.20
2.900	0.574	0.0237	11.84
3.000	0.630	0.0260	12.58
3.100	0.690	0.0285	13.32
3.200	0.765	0.0316	14.20
3.300	0.860	0.0356	15.25
3.400	0.970	0.0401	16.34
3.500	1.120	0.0463	17.65
3.600	1.305	0.0539	19.12
3.700	1.530	0.0633	20.72
3.800	1.785	0.0738	22.33
3.900	2.070	0.0856	23.91

Table 2. Benzene on Graphite at 273.16° K
 $P^0 = 24.19$ mm of Mercury (Concluded)

W_a mg/gm	P mm of Hg	$\frac{P}{P^0}$	Π dynes/cm
4.000	2.385	0.0986	25.44
4.100	2.730	0.113	26.91
4.200	3.155	0.130	28.51
4.300	3.650	0.151	30.17
4.400	4.225	0.175	31.90
4.500	4.860	0.201	33.61
4.600	5.565	0.230	35.30
4.700	6.270	0.259	36.80
4.800	6.920	0.289	38.05
4.900	7.535	0.311	39.18
5.000	8.110	0.335	40.17
5.200	9.15	0.378	41.84
5.400	10.15	0.420	43.33
5.600	11.10	0.459	44.67
5.800	11.95	0.494	45.81
6.000	12.65	0.523	46.72
6.200	13.20	0.546	47.42
6.400	13.65	0.564	48.00
6.600	14.00	0.579	48.44
6.800	14.35	0.593	48.89
7.000	14.65	0.606	49.28
7.200	15.00	0.620	49.73
7.400	15.25	0.630	50.06
7.600	15.50	0.641	50.39
7.800	15.75	0.651	50.73
8.000	16.00	0.661	51.07
8.200	16.25	0.672	51.41
8.400	16.60	0.686	51.89
8.600	16.95	0.701	52.37
8.800	17.30	0.715	52.85
9.000	17.65	0.730	53.33
9.250	18.15	0.750	54.02
9.500	18.60	0.769	54.65
9.750	18.90	0.781	55.06
10.000	19.35	0.800	55.69
10.500	20.00	0.827	56.61
11.000	20.60	0.852	57.48
11.500	21.10	0.872	58.21
12.000	21.45	0.887	58.74
12.500	21.80	0.901	59.28
13.000	22.15	0.916	59.82
13.500	22.55	0.932	60.46
14.000	22.90	0.947	61.04

Table 3. Benzene on Graphite at 288.16° K
 $P^0 = 58.83$ mm of Mercury

W_a mg/gm	P mm of Hg	$\frac{P}{P^0}$	Π dynes/cm
0.100	0.023	0.000391	0.30
0.200	0.046	0.000782	0.58
0.300	0.072	0.00122	0.90
0.400	0.097	0.00165	1.20
0.500	0.124	0.00210	1.52
0.600	0.152	0.00258	1.84
0.700	0.183	0.00311	2.18
0.800	0.218	0.00371	2.55
0.900	0.254	0.00432	2.93
1.000	0.291	0.00495	3.30
1.100	0.330	0.00561	3.67
1.200	0.372	0.00632	4.07
1.300	0.418	0.00711	4.49
1.400	0.464	0.00789	4.89
1.500	0.510	0.00867	5.28
1.600	0.556	0.00945	5.66
1.700	0.603	0.0103	6.05
1.800	0.649	0.0110	6.42
1.900	0.695	0.0118	6.78
2.000	0.743	0.0126	7.15
2.100	0.797	0.0135	7.56
2.200	0.857	0.0146	8.01
2.300	0.938	0.0158	8.59
2.400	1.021	0.0172	9.16
2.500	1.117	0.0190	9.79
2.600	1.217	0.0208	10.42
2.700	1.330	0.0226	11.09
2.800	1.443	0.0245	11.73
2.900	1.573	0.0267	12.44
3.000	1.732	0.0294	13.25
3.100	1.920	0.0326	14.15
3.200	2.140	0.0364	15.13
3.300	2.415	0.0411	16.25
3.400	2.750	0.0468	17.50
3.500	3.135	0.0533	18.79
3.600	3.595	0.0611	20.19
3.700	4.155	0.0706	21.71
3.800	4.835	0.0822	23.34
3.900	5.615	0.0955	24.99

Table 3. Benzene on Graphite at 288.16° K

 $P^0 = 58.83$ mm of Mercury (Concluded)

W_a mg/gm	P mm of Hg	$\frac{P}{P^0}$	Π dynes/cm
4.000	6.495	0.110	26.63
4.100	7.390	0.126	28.12
4.200	8.400	0.143	29.64
4.300	9.500	0.162	31.14
4.400	10.70	0.182	32.63
4.500	11.90	0.202	33.97
4.600	13.20	0.224	35.33
4.700	14.45	0.246	36.53
4.800	15.80	0.269	37.74
4.900	17.20	0.292	38.91
5.000	18.55	0.315	39.98
5.200	21.00	0.357	41.79
5.400	23.20	0.394	43.32
5.600	25.00	0.425	44.50
5.800	26.45	0.450	45.42
6.000	27.85	0.473	46.28
6.200	29.05	0.494	47.01
6.400	30.10	0.512	47.66
6.600	31.10	0.529	48.26
6.800	32.00	0.544	48.81
7.000	32.85	0.558	49.33
7.200	33.65	0.572	49.82
7.400	34.45	0.586	50.31
7.600	35.25	0.599	50.80
7.800	36.05	0.613	51.29
8.000	36.80	0.626	51.76
8.200	37.50	0.638	52.20
8.400	38.20	0.649	52.64
8.600	38.90	0.661	53.08
8.800	39.60	0.673	53.52
9.000	40.25	0.684	53.94
9.250	41.10	0.699	54.48
9.500	41.95	0.713	55.03
9.750	42.80	0.728	55.59
10.000	43.65	0.742	56.14
10.500	45.20	0.768	57.16
11.000	46.50	0.791	58.02
11.500	47.50	0.808	58.71
12.000	48.40	0.823	59.34
12.500	49.10	0.835	59.85
13.000	49.70	0.845	60.29
13.500	50.25	0.854	60.71
14.000	50.85	0.864	61.18

Table 4. Benzene on Graphite at 298.16° K
 $P^{\circ} = 95.18$ mm of Mercury

W_a mg/gm	P mm of Hg	$\frac{P}{P^{\circ}}$	Π dynes/cm
0.043	0.020	0.000210	0.12
0.100	0.048	0.000504	0.30
0.124	0.060	0.000631	0.37
0.164	0.080	0.000841	0.49
0.200	0.098	0.00103	0.60
0.242	0.120	0.00126	0.73
0.281	0.140	0.00147	0.85
0.300	0.161	0.00169	0.97
0.400	0.205	0.00215	1.22
0.500	0.265	0.00279	1.56
0.556	0.300	0.00315	1.76
0.600	0.327	0.00344	1.90
0.700	0.390	0.00410	2.24
0.800	0.453	0.00476	2.57
0.900	0.516	0.00542	2.90
0.955	0.550	0.00578	3.08
1.000	0.578	0.00607	3.22
1.035	0.600	0.00631	3.33
1.100	0.641	0.00674	3.54
1.200	0.707	0.00743	3.88
1.300	0.783	0.00823	4.25
1.344	0.820	0.00862	4.43
1.400	0.865	0.00909	4.65
1.440	0.900	0.00946	4.82
1.500	0.952	0.0100	5.06
1.554	1.000	0.0105	5.29
1.600	1.044	0.0110	5.49
1.700	1.149	0.0121	5.95
1.800	1.261	0.0133	6.44
1.900	1.365	0.0143	6.87
2.000	1.485	0.0156	7.36
2.100	1.620	0.0170	7.89
2.200	1.737	0.0183	8.33
2.300	1.866	0.0196	8.81
2.400	2.010	0.0211	9.33
2.500	2.170	0.0228	9.88
2.600	2.345	0.0246	10.46
2.700	2.545	0.0267	11.10
2.800	2.750	0.0289	11.74
2.900	2.985	0.0314	12.43

Table 4. Benzene on Graphite at 298.16° K
 $P^{\circ} = 95.18$ mm of Mercury (Concluded)

W_a mg/gm	P mm of Hg	$\frac{P}{P^{\circ}}$	Π dynes/cm
3.000	3.235	0.0340	13.13
3.100	3.515	0.0369	13.88
3.200	3.850	0.0405	14.73
3.300	4.280	0.0450	15.75
3.400	4.885	0.0513	17.06
3.500	5.555	0.0584	18.39
3.600	6.290	0.0661	19.69
3.700	7.240	0.0761	21.21
3.800	8.390	0.0882	22.84
3.900	9.645	0.101	24.43
4.000	11.05	0.116	26.02
4.100	12.65	0.133	27.65
4.200	14.35	0.151	29.19
4.300	16.20	0.170	30.72
4.400	18.30	0.192	32.29
4.500	20.55	0.216	33.81
4.600	22.60	0.236	35.09
4.700	24.65	0.259	36.29
4.800	26.70	0.282	37.41
4.900	28.70	0.302	38.45
5.000	30.55	0.322	39.37
5.200	34.05	0.358	41.01
5.400	37.00	0.389	42.31
5.600	39.75	0.418	43.47
5.800	42.35	0.445	44.54
6.000	44.85	0.471	45.54
6.200	47.10	0.495	46.41
6.400	48.95	0.514	47.13
6.600	50.60	0.532	47.76
6.800	52.10	0.548	48.33
7.000	53.55	0.563	48.89
7.200	54.90	0.577	49.40
7.400	56.25	0.591	49.92
7.600	57.55	0.605	50.42
7.800	58.80	0.618	50.90
8.000	60.05	0.631	51.39
8.200	61.00	0.642	51.77
8.400	61.85	0.650	52.11
8.600	62.60	0.658	52.41
8.800	63.30	0.665	52.70
9.000	64.00	0.673	52.99
9.250	64.75	0.681	53.31
9.500	65.50	0.688	53.63
9.750	66.20	0.696	53.93

Table 5. Benzene on Graphite at 303.16° K
 $P^0 = 119.31$ mm of Mercury

W_a mg/gm	P mm of Hg	$\frac{P}{P^0}$	Π dynes/cm
0.022	0.020	0.000168	0.07
0.044	0.040	0.000335	0.12
0.067	0.060	0.000503	0.18
0.100	0.086	0.000721	0.27
0.117	0.100	0.000838	0.32
0.154	0.125	0.00105	0.42
0.200	0.153	0.00128	0.53
0.240	0.175	0.00147	0.61
0.300	0.215	0.00180	0.78
0.347	0.250	0.00210	0.92
0.400	0.291	0.00244	1.09
0.446	0.325	0.00272	1.23
0.500	0.364	0.00305	1.40
0.548	0.400	0.00335	1.55
0.600	0.440	0.00369	1.71
0.651	0.480	0.00402	1.87
0.700	0.518	0.00434	2.03
0.738	0.550	0.00461	2.16
0.800	0.603	0.00505	2.38
0.843	0.640	0.00536	2.52
0.900	0.689	0.00578	2.71
1.000	0.774	0.00649	3.05
1.030	0.800	0.00671	3.15
1.100	0.860	0.00721	3.38
1.147	0.900	0.00754	3.53
1.200	0.945	0.00792	3.70
1.265	1.000	0.00838	3.91
1.300	1.030	0.00863	4.03
1.400	1.114	0.00934	4.35
1.500	1.207	0.0101	4.70
1.600	1.311	0.0110	5.08
1.700	1.425	0.0119	5.49
1.800	1.562	0.0131	5.97
1.900	1.709	0.0143	6.48
2.000	1.855	0.0155	6.96
2.100	2.005	0.0168	7.44
2.200	2.175	0.0182	7.97
2.300	2.355	0.0197	8.51
2.400	2.550	0.0214	9.07

Table 5. Benzene on Graphite at 303.16° K
 $P^{\circ} = 119.31$ mm of Mercury (Concluded)

W_a mg/gm	P mm of Hg	$\frac{P}{P^{\circ}}$	Π dynes/cm
2.500	2.785	0.0233	9.72
2.600	3.045	0.0255	10.40
2.700	3.335	0.0280	11.13
2.800	3.655	0.0306	11.89
2.900	4.005	0.0336	12.67
3.000	4.400	0.0369	13.51
3.100	4.905	0.0411	14.51
3.200	5.525	0.0463	15.64
3.300	6.250	0.0524	16.85
3.400	7.080	0.0593	18.11
3.500	7.990	0.0670	19.36
3.600	9.045	0.0758	20.68
3.700	10.24	0.0858	22.05
3.800	11.65	0.0977	23.51
3.900	13.25	0.111	25.00
4.000	15.05	0.126	26.51
4.100	17.00	0.142	28.00
4.200	19.25	0.161	29.55
4.300	21.55	0.181	31.00
4.400	23.95	0.201	32.39
4.500	26.45	0.222	33.72
4.600	29.00	0.243	34.98
4.700	31.70	0.266	36.22
4.800	34.50	0.289	37.43
4.900	37.10	0.311	38.49
5.000	39.60	0.332	39.47
5.200	44.00	0.369	41.09
5.400	47.75	0.400	42.39
5.600	51.35	0.430	43.59
5.800	54.60	0.458	44.65
6.000	57.35	0.481	45.52
6.200	59.65	0.500	46.24
6.400	61.85	0.518	46.92
6.600	64.90	0.544	47.87
6.800	66.85	0.560	48.47
7.000	67.80	0.568	48.76
7.200	69.65	0.584	49.34
7.400	71.40	0.598	49.88
7.600	73.10	0.613	50.41
7.800	74.70	0.626	50.91
8.000	76.30	0.640	51.42
8.200	77.85	0.653	51.91
8.400	79.35	0.665	52.39

Table 6. Benzene on Graphite at 323.16° K
 $P^{\circ} = 271.23$ mm of Mercury

W_a mg/gm	P mm of Hg	$\frac{P}{P^{\circ}}$	Π dynes/cm
0.040	0.083	0.000306	0.10
0.080	0.151	0.000557	0.21
0.120	0.209	0.000771	0.32
0.160	0.266	0.000981	0.43
0.200	0.328	0.00121	0.55
0.240	0.399	0.00147	0.68
0.280	0.473	0.00174	0.83
0.320	0.553	0.00204	0.98
0.360	0.635	0.00234	1.13
0.400	0.718	0.00265	1.28
0.440	0.801	0.00295	1.42
0.480	0.884	0.00326	1.57
0.520	0.967	0.00356	1.71
0.538	1.000	0.00369	1.77
0.600	1.139	0.00420	2.01
0.700	1.364	0.00503	2.39
0.800	1.568	0.00578	2.72
0.900	1.777	0.00655	3.06
1.000	2.010	0.00741	3.44
1.100	2.260	0.00833	3.83
1.200	2.505	0.00923	4.21
1.300	2.765	0.0102	4.61
1.400	3.040	0.0112	5.02
1.500	3.345	0.0123	5.46
1.600	3.665	0.0135	5.92
1.700	4.010	0.0148	6.40
1.800	4.370	0.0161	6.88
1.900	4.745	0.0175	7.37
2.000	5.170	0.0191	7.91
2.100	5.635	0.0208	8.47
2.200	6.125	0.0226	9.05
2.300	6.645	0.0245	9.64
2.400	7.180	0.0265	10.22
2.500	7.800	0.0288	10.87
2.600	8.525	0.0314	11.60
2.700	9.340	0.0344	12.37
2.800	10.25	0.0383	13.19
2.900	11.30	0.0422	14.09
3.000	12.60	0.0464	15.12

Table 6. Benzene on Graphite at 323.16° K

$P^{\circ} = 271.23$ mm of Mercury
(Concluded)

W_a mg/gm	P mm of Hg	$\frac{P}{P^{\circ}}$	Π dynes/cm
3.100	13.85	0.0511	16.04
3.200	15.60	0.0575	17.25
3.300	17.10	0.0630	18.21
3.400	19.25	0.0710	19.48
3.500	21.10	0.0778	20.49
3.600	24.50	0.0903	22.20
3.700	27.75	0.102	23.67
3.800	31.30	0.115	25.13
3.900	35.05	0.129	26.53
4.000	39.10	0.144	27.91
4.100	43.60	0.161	29.32
4.200	48.75	0.180	30.80
4.300	53.75	0.198	32.13
4.400	58.85	0.217	33.40
4.500	63.95	0.236	34.59
4.600	68.95	0.254	35.69
4.700	74.05	0.273	36.76
4.800	79.10	0.292	37.76

Table 7. Benzene on Boron Nitride at 273.16° K
 $P^0 = 24.19$ mm of Mercury

W_a mg/gm	P mm of Hg	$\frac{P}{P^0}$	Π dynes/cm
0.100	0.001	0.0000413	0.02
0.200	0.008	0.000331	0.15
0.300	0.022	0.000909	0.40
0.400	0.042	0.00174	0.73
0.500	0.067	0.00277	1.10
0.600	0.095	0.00393	1.46
0.675	0.120	0.00496	1.74
0.729	0.140	0.00579	1.95
0.780	0.160	0.00661	2.14
0.829	0.180	0.00744	2.31
0.874	0.200	0.00827	2.48
0.960	0.240	0.00992	2.79
1.039	0.280	0.0116	3.07
1.112	0.320	0.0132	3.33
1.216	0.380	0.0157	3.69
1.317	0.440	0.0182	4.03
1.421	0.500	0.0208	4.35
1.521	0.560	0.0232	4.66
1.625	0.620	0.0256	4.96
1.728	0.680	0.0281	5.24
1.833	0.740	0.0306	5.52
1.934	0.800	0.0331	5.79
2.071	0.880	0.0364	6.14
2.192	0.950	0.0393	6.44
2.275	1.000	0.0413	6.65
2.300	1.015	0.0420	6.72
2.400	1.075	0.0444	6.96
2.500	1.145	0.0473	7.25
2.600	1.210	0.0500	7.51
2.700	1.275	0.0527	7.76
2.800	1.350	0.0550	8.05
2.900	1.420	0.0587	8.32
3.000	1.490	0.0616	8.58
3.100	1.570	0.0649	8.87
3.200	1.650	0.0682	9.16
3.300	1.735	0.0717	9.46
3.400	1.820	0.0752	9.76
3.500	1.910	0.0740	10.06
3.600	2.000	0.0827	10.36

Table 7. Benzene on Boron Nitride at 273.16° K

 $P^{\circ} = 24.19$ mm of Mercury (Continued)

W_a mg/gm	P mm of Hg	$\frac{P}{P^{\circ}}$	Π dynes/cm
3.700	2.095	0.0866	10.67
3.800	2.190	0.0905	10.98
3.900	2.295	0.0949	11.31
4.000	2.415	0.0998	11.68
4.100	2.540	0.105	12.06
4.200	2.675	0.111	12.45
4.300	2.815	0.116	12.85
4.400	2.970	0.123	13.28
4.500	3.130	0.129	13.71
4.600	3.280	0.136	14.10
4.700	3.455	0.143	14.55
4.800	3.625	0.150	14.90
4.900	3.795	0.157	15.38
5.000	3.975	0.164	15.80
5.100	4.155	0.172	16.21
5.200	4.330	0.179	16.60
5.300	4.525	0.187	17.03
5.400	4.710	0.195	17.42
5.500	4.905	0.203	17.83
5.600	5.110	0.211	18.25
5.700	5.315	0.220	18.66
5.800	5.530	0.229	19.08
5.900	5.745	0.237	19.49
6.000	5.965	0.247	19.90
6.100	6.185	0.256	20.30
6.200	6.405	0.265	20.70
6.300	6.630	0.274	21.10
6.400	6.860	0.284	21.50
6.500	7.080	0.293	21.87
6.600	7.295	0.302	22.23
6.800	7.735	0.320	22.96
7.000	8.165	0.338	23.64
7.200	8.610	0.356	24.34
7.400	9.035	0.374	24.98
7.600	9.485	0.392	25.65
7.800	9.950	0.411	26.33
8.000	10.45	0.432	27.05
8.200	10.95	0.453	27.74
8.400	11.40	0.471	28.36
8.600	11.85	0.490	28.96
8.800	12.15	0.502	29.37
9.000	12.45	0.515	29.77

Table 7. Benzene on Boron Nitride at 273.16° K
 $P^0 = 24.19$ mm of Mercury (Concluded)

W_a mg/gm	P mm of Hg	$\frac{P}{P^0}$	Π dynes/cm
9.250	12.80	0.529	30.23
9.500	13.15	0.544	30.70
9.750	13.45	0.556	31.10
10.000	13.75	0.568	31.50
10.250	14.10	0.583	31.97
10.500	14.65	0.606	32.70
10.750	14.85	0.614	32.96
11.000	15.15	0.626	33.36
11.500	15.75	0.651	34.17
12.000	16.25	0.672	34.84
12.500	16.65	0.688	35.39
13.000	16.85	0.697	35.67

Table 8. Benzene on Boron Nitride at 288.16° K
 $P^0 = 58.83$ mm of Mercury

W_a mg/gm	P mm of Hg	$\frac{P}{P^0}$	Π dynes/cm
0.050	0.010	0.000170	0.08
0.103	0.024	0.000408	0.19
0.162	0.044	0.000748	0.34
0.224	0.068	0.00116	0.50
0.292	0.100	0.00170	0.70
0.368	0.140	0.00238	0.92
0.448	0.180	0.00306	1.11
0.528	0.244	0.00415	1.40
0.627	0.320	0.00544	1.70
0.718	0.400	0.00680	1.99
0.802	0.480	0.00816	2.26
0.881	0.560	0.00952	2.51
0.957	0.640	0.0109	2.75
1.029	0.720	0.0122	2.98
1.100	0.800	0.0136	3.20
1.183	0.900	0.0153	3.46
1.266	1.000	0.0170	3.71
1.300	1.040	0.0177	3.80
1.400	1.170	0.0199	4.11
1.500	1.290	0.0219	4.38
1.600	1.415	0.0241	4.66
1.700	1.545	0.0263	4.94
1.800	1.685	0.0286	5.23
1.900	1.830	0.0311	5.53
2.000	1.980	0.0337	5.83
2.100	2.135	0.0363	6.13
2.200	2.300	0.0391	6.44
2.300	2.465	0.0419	6.75
2.400	2.635	0.0448	7.06
2.500	2.805	0.0477	7.36
2.600	2.965	0.0504	7.63
2.700	3.130	0.0532	7.91
2.800	3.300	0.0561	8.20
2.900	3.475	0.0591	8.48
3.000	3.655	0.0621	8.77
3.100	3.845	0.0654	9.07
3.200	4.035	0.0686	9.36
3.300	4.240	0.0721	9.67
3.400	4.465	0.0759	10.00

Table 8. Benzene on Boron Nitride at 288.16° K
 $P^{\circ} = 58.83$ mm of Mercury (Continued)

W_a mg/gm	P mm of Hg	$\frac{P}{P^{\circ}}$	Π dynes/cm
3.500	4.705	0.0800	10.35
3.600	4.970	0.0845	10.73
3.700	5.230	0.0889	11.09
3.800	5.510	0.0937	11.47
3.900	5.795	0.0985	11.85
4.000	6.085	0.103	12.23
4.100	6.380	0.108	12.60
4.300	6.990	0.119	13.35
4.500	7.655	0.130	14.12
4.700	8.450	0.144	15.00
4.900	9.340	0.159	15.93
5.100	10.35	0.176	16.93
5.200	10.80	0.184	17.36
5.300	11.30	0.192	17.82
5.400	11.85	0.201	18.31
5.500	12.35	0.210	18.75
5.600	12.90	0.219	19.22
5.700	13.40	0.228	19.64
5.800	13.90	0.236	20.05
5.900	14.40	0.245	20.45
6.000	14.90	0.253	20.84
6.100	15.40	0.262	21.23
6.200	15.85	0.269	21.58
6.300	16.25	0.276	21.88
6.400	16.75	0.285	22.25
6.500	17.25	0.293	22.62
6.600	17.75	0.302	22.98
6.800	18.80	0.320	23.73
7.000	19.85	0.337	24.46
7.200	20.85	0.354	25.14
7.400	21.85	0.371	25.80
7.600	22.80	0.388	26.42
7.800	23.70	0.403	27.00
8.000	24.55	0.417	27.54
8.200	25.40	0.432	28.08
8.400	26.25	0.446	28.61
8.600	27.10	0.461	29.13
8.800	27.85	0.473	29.60
9.000	28.60	0.486	30.06
9.250	29.50	0.502	30.60
9.500	30.30	0.515	31.09
9.750	31.15	0.530	31.61

Table 8. Benzene on Boron Nitride at 288.16° K
 $P^{\circ} = 58.83$ mm of Mercury (Concluded)

W_a mg/gm	P mm of Hg	$\frac{P}{P^{\circ}}$	Π dynes/cm
10.000	31.95	0.543	32.10
10.250	32.65	0.555	32.52
10.500	33.40	0.568	32.98
10.750	34.05	0.579	33.38
11.000	34.70	0.590	33.78
11.500	35.85	0.609	34.49
12.000	36.85	0.626	35.12
12.500	37.85	0.643	35.75
13.000	38.70	0.658	36.30

Table 9. Benzene on Boron Nitride at 298.16° K
 $P^0 = 95.18$ mm of Mercury

W_a mg/gm	P mm of Hg	$\frac{P}{P^0}$	Π dynes/cm
0.050	0.012	0.000126	0.09
0.100	0.026	0.000273	0.19
0.150	0.048	0.000504	0.33
0.193	0.072	0.000757	0.46
0.235	0.100	0.00105	0.61
0.277	0.132	0.00139	0.75
0.319	0.168	0.00177	0.90
0.358	0.208	0.00219	1.04
0.398	0.252	0.00265	1.19
0.438	0.300	0.00315	1.33
0.480	0.351	0.00369	1.48
0.526	0.408	0.00429	1.63
0.574	0.468	0.00492	1.78
0.621	0.532	0.00559	1.94
0.669	0.596	0.00626	2.08
0.718	0.664	0.00698	2.23
0.769	0.736	0.00774	2.39
0.826	0.820	0.00862	2.56
0.882	0.908	0.00954	2.74
0.941	1.000	0.0105	2.91
1.000	1.110	0.0117	3.11
1.100	1.300	0.0137	3.44
1.200	1.520	0.0160	3.80
1.300	1.740	0.0183	4.14
1.400	1.975	0.0208	4.49
1.500	2.210	0.0232	4.82
1.600	2.445	0.0257	5.14
1.700	2.685	0.0282	5.45
1.800	2.930	0.0308	5.76
1.900	3.175	0.0334	6.06
2.000	3.430	0.0360	6.36
2.100	3.680	0.0387	6.65
2.200	3.945	0.0415	6.95
2.300	4.215	0.0443	7.24
2.400	4.495	0.0472	7.55
2.500	4.780	0.0502	7.85
2.600	5.065	0.0532	8.15
2.700	5.350	0.0562	8.44
2.800	5.655	0.0594	8.75

Table 9. Benzene on Boron Nitride at 298.16° K
 $P^{\circ} = 95.18$ mm of Mercury (Continued)

W_a mg/gm	P mm of Hg	$\frac{P}{P^{\circ}}$	Π dynes/cm
2.900	5.985	0.0629	9.07
3.000	6.330	0.0665	9.40
3.100	6.670	0.0701	9.73
3.200	7.030	0.0739	10.05
3.400	7.755	0.0815	10.70
3.600	8.615	0.0905	11.45
3.800	9.595	0.101	12.24
4.000	10.65	0.112	13.06
4.100	11.25	0.118	13.51
4.200	11.80	0.124	13.90
4.300	12.40	0.130	14.33
4.400	13.00	0.137	14.74
4.500	13.60	0.143	15.14
4.600	14.25	0.150	15.57
4.700	14.85	0.156	15.95
4.800	15.55	0.163	16.39
4.900	16.20	0.170	16.79
5.000	16.95	0.178	17.25
5.100	17.70	0.186	17.69
5.200	18.45	0.194	18.12
5.300	19.25	0.202	18.56
5.400	20.05	0.211	19.00
5.500	20.85	0.219	19.43
5.600	21.70	0.228	19.87
5.700	22.55	0.237	20.31
5.800	23.40	0.246	20.74
5.900	24.25	0.255	21.16
6.000	25.15	0.264	21.59
6.100	26.00	0.273	22.00
6.200	26.85	0.282	22.40
6.300	27.65	0.290	22.76
6.400	28.50	0.300	23.15
6.500	29.30	0.308	23.51
6.600	30.10	0.316	23.86
6.800	31.65	0.333	24.54
7.000	33.25	0.349	25.22
7.200	34.80	0.367	25.87
7.400	36.35	0.382	26.51
7.600	37.85	0.398	27.12
7.800	39.30	0.413	27.70
8.000	40.75	0.428	28.28
8.200	42.10	0.442	28.81

Table 9. Benzene on Boron Nitride at 298.16° K

 $P^0 = 95.18$ mm of Mercury (Concluded)

W_a mg/gm	P mm of Hg	$\frac{P}{P^0}$	Π dynes/cm
8.400	43.45	0.457	29.34
8.600	44.80	0.471	29.86
8.800	46.05	0.484	30.34
9.000	47.20	0.497	30.78
9.250	48.55	0.510	31.30
9.500	49.80	0.523	31.78
9.750	51.00	0.537	32.24
10.000	52.20	0.549	32.70
10.250	53.45	0.562	33.18
10.500	54.65	0.574	33.64
10.750	55.85	0.587	34.11
11.000	56.90	0.598	34.52
11.500	58.85	0.619	35.28
12.000	60.60	0.637	35.97
12.500	62.15	0.653	36.59
13.000	63.55	0.668	37.16

Table 10. Benzene on Boron Nitride at 303.16° K
 $P^0 = 119.31$ mm of Mercury

W_a mg/gm	P mm of Hg	$\frac{P}{P^0}$	Π dynes/cm
0.018	0.018	0.000151	0.10
0.133	0.047	0.000394	0.24
0.180	0.082	0.000687	0.40
0.220	0.118	0.000989	0.55
0.253	0.154	0.00129	0.68
0.292	0.203	0.00170	0.83
0.328	0.260	0.00218	0.99
0.365	0.317	0.00266	1.13
0.404	0.374	0.00313	1.26
0.439	0.431	0.00361	1.38
0.480	0.468	0.00392	1.46
0.526	0.560	0.00469	1.64
0.570	0.640	0.00536	1.79
0.613	0.720	0.00604	1.94
0.658	0.800	0.00671	2.07
0.711	0.900	0.00754	2.24
0.761	1.000	0.00838	2.40
0.800	1.080	0.00905	2.52
0.900	1.290	0.0108	2.82
1.000	1.525	0.0128	3.15
1.100	1.780	0.0149	3.48
1.200	2.050	0.0182	3.82
1.300	2.335	0.0196	4.15
1.400	2.630	0.0220	4.48
1.500	2.930	0.0246	4.80
1.600	3.230	0.0271	5.11
1.700	3.535	0.0296	5.42
1.800	3.845	0.0322	5.71
1.900	4.175	0.0350	6.02
2.000	4.515	0.0378	6.33
2.100	4.870	0.0408	6.65
2.200	5.240	0.0439	6.97
2.300	5.610	0.0470	7.29
2.400	5.995	0.0503	7.61
2.500	6.390	0.0529	7.93
2.600	6.780	0.0568	8.24
2.700	7.175	0.0601	8.54
2.800	7.590	0.0636	8.86

Table 10. Benzene on Boron Nitride at 303.16° K

$P^0 = 119.31$ mm of Mercury
(Continued)

W_a mg/gm	P mm of Hg	$\frac{P}{P^0}$	Π dynes/cm
3.000	8.475	0.0710	9.51
3.200	9.410	0.0789	10.17
3.400	10.45	0.0876	10.88
3.500	11.10	0.0930	11.30
3.600	11.75	0.0985	11.72
3.700	12.35	0.104	12.09
3.800	13.00	0.109	12.48
3.900	13.70	0.115	12.89
4.000	14.45	0.121	13.32
4.100	15.20	0.127	13.74
4.200	15.95	0.134	14.15
4.300	16.70	0.140	14.55
4.400	17.50	0.147	14.96
4.500	18.35	0.154	15.40
4.600	19.15	0.161	15.79
4.700	19.95	0.167	16.18
4.800	20.80	0.174	16.59
4.900	21.65	0.181	16.98
5.000	22.55	0.189	17.40
5.100	23.50	0.197	17.82
5.200	24.45	0.205	18.24
5.300	25.45	0.213	18.67
5.400	26.50	0.222	19.11
5.500	27.55	0.231	19.54
5.600	28.60	0.240	19.97
5.700	29.70	0.249	20.40
5.800	30.80	0.258	20.83
5.900	31.95	0.268	21.27
6.000	33.05	0.277	21.68
6.100	34.15	0.286	22.08
6.200	35.20	0.295	22.47
6.300	36.30	0.304	22.86
6.400	37.35	0.313	23.23
6.500	38.35	0.321	23.58
6.600	39.35	0.330	23.92
6.800	41.50	0.348	24.65
7.000	43.70	0.366	25.38
7.200	45.75	0.383	26.04
7.400	47.70	0.400	26.66
7.600	49.55	0.415	27.25
7.800	51.35	0.430	27.81

Table 10. Benzene on Boron Nitride at 303.16° K

$P^0 = 119.31$ mm of Mercury
(Concluded)

W_a mg/gm	P mm of Hg	$\frac{P}{P^0}$	Π dynes/cm
8.000	53.05	0.445	28.33
8.200	54.80	0.459	28.87
8.400	56.45	0.473	29.38
8.600	58.05	0.487	29.86
8.800	59.65	0.500	30.34
9.000	61.15	0.513	30.80
9.250	62.90	0.527	31.32
9.500	64.60	0.541	31.83
9.750	66.25	0.555	32.33
10.000	67.85	0.569	32.81
10.250	69.40	0.583	33.28
10.500	70.90	0.594	33.73
10.750	72.35	0.606	34.17
11.000	73.80	0.619	34.61

Table 11. Isosteric Heats of Benzene on Graphite at 298.16° K

W_a	ΔC_P^{st} cal/° K-mole	ΔH^{st} kcal/mole
0.20	(4.41)	(10.20)
0.40	5.32	11.63
0.60	5.14	10.98
0.80	5.04	10.57
1.00	4.98	10.30
1.20	4.99	10.19
1.40	5.01	10.13
1.60	5.09	10.16
1.80	5.18	10.26
2.00	5.27	10.34
2.20	5.36	10.42
2.40	5.34	10.29
2.60	5.28	10.09
2.80	5.52	10.45
3.00	5.62	10.54
3.20	5.72	10.61
3.40	5.74	10.52
3.60	5.72	10.31
3.80	5.67	10.06
4.00	5.62	9.80
4.20	5.60	9.61
4.40	5.49	9.25
4.60	5.49	9.12
4.80	5.41	8.86
5.00	5.38	8.72
5.20	5.37	8.63
5.40	5.33	8.50
5.60	5.30	8.40
5.80	5.29	8.34
6.00	5.30	8.32
6.20	5.31	8.32
6.40	5.33	8.34
6.60	5.39	8.44
6.80	5.42	8.47
7.00	5.42	8.56
7.20	5.43	8.47
7.40	5.46	8.52
7.60	5.49	8.56
7.80	5.51	8.59

Table 11. Isosteric Heats of Benzene on Graphite at 298.16° K
(Concluded)

W_a	ΔC_P^{st}	ΔH^{st}
	cal/° K-mole	kcal/mole
8.00	5.53	8.62
8.20	5.54	8.64
8.40	5.54	8.61
8.60	5.51	8.55
8.80	5.48	8.49
9.00	5.46	8.44
9.25	5.41	8.33
9.50	5.38	8.25
9.75	5.37	8.23

Note: From $W_a = 0.1$ to 4.5 -- 5 isotherms used in calculation
 $W_a = 4.5$ to 8.4 -- 4 isotherms used in calculation --
no 50° C isotherms
 $W_a = 8.4$ to 9.75 -- 3 isotherms used in calculation --
no 50° C or 30° C isotherms

All ΔC_P^{st} and ΔH^{st} at 298.16° K used the 50° C, 30° C, 25° C, 15° C, and 0° C isotherms for benzene on graphite except where noted.

Table 12. Isosteric Heats of Benzene on Boron Nitride at 298.16° K

w_a	ΔC_P^{st} cal/° K-mole	ΔH^{st} kcal/mole
0.200	(5.13)	(11.86)
0.400	(5.48)	(11.71)
0.600	5.24	10.86
0.800	5.01	10.13
1.000	4.85	9.59
1.200	4.84	9.41
1.400	4.82	9.22
1.600	4.87	9.20
1.800	4.93	9.21
2.000	5.01	9.27
2.200	5.09	9.35
2.400	5.17	9.43
2.600	5.22	9.45
2.800	5.26	9.47
3.000	5.33	9.54
3.200	5.37	9.56
3.400	5.41	9.59
3.600	5.50	9.69
3.800	5.59	9.81
4.000	5.62	9.81
4.200	5.64	9.81
4.400	5.65	9.75
4.600	5.65	9.70
4.800	5.63	9.60
5.000	5.62	9.54
5.200	5.63	9.51
5.400	5.55	9.50
5.600	5.66	9.46
5.800	5.67	9.44
6.000	5.67	9.42
6.200	5.67	9.38
6.400	5.67	9.33
6.600	5.66	9.28
6.800	5.65	9.24
7.000	5.66	9.22
7.200	5.65	9.18
7.400	5.65	9.14
7.600	5.63	9.09
7.800	5.61	9.02
8.000	5.58	8.94

Table 12. Isosteric Heats of Benzene on Boron Nitride at 298.16° K
(Concluded)

W_a	ΔC_P^{st}	ΔH^{st}
	cal/° K-mole	kcal/mole
8.200	5.55	8.86
8.400	5.53	8.80
8.600	5.51	8.74
8.800	5.52	8.76
9.000	5.53	8.76
9.250	5.54	8.76
9.500	5.55	8.75
9.750	5.56	8.76
10.000	5.57	8.77
10.250	5.57	8.76
10.500	5.53	8.67
10.750	5.56	8.71
11.000	5.56	8.71
11.500	5.52	8.61
12.000	5.52	8.60
12.500	5.53	8.60
13.000	5.58	8.68

Note: The 30° C, 25° C, 15° C, and 0° C isotherms were used in the calculations except above $W_a = 11.000$ mg/gm of sample when the 30° C isotherm dropped out.

Table 13. ΔC_p^{ads} , ΔH^{ads} , ΔG^{ads} , and ΔS^{ads} of Benzene on Graphite
at 298.16° K

Π dynes/cm	ΔC_p^{ads} cal/° K-mole	ΔH^{ads} kcal/mole	$-\Delta G^{\text{ads}}$ kcal/mole	$-\Delta S^{\text{ads}}$ cal/° K-mole
0.500	5.05	11.59	54.19	20.70
1.000	4.84	10.74	49.87	19.30
1.500	4.78	10.39	47.39	18.94
2.000	4.88	10.42	45.59	19.65
2.500	4.90	10.31	44.15	19.77
3.000	4.91	10.22	43.00	19.85
3.500	5.00	10.31	42.03	20.47
4.000	5.03	10.26	41.15	20.61
4.500	5.00	10.12	40.37	20.41
5.500	4.98	9.96	39.04	20.31
6.000	4.99	9.91	38.42	20.36
6.500	5.02	9.91	37.85	20.55
7.000	5.03	9.88	37.33	20.62
7.500	5.04	9.85	36.82	20.69
8.000	5.03	9.78	36.33	20.62
8.500	5.04	9.77	35.90	20.71
9.000	5.05	9.74	35.45	20.77
9.500	5.07	9.72	35.03	20.86
10.000	5.08	9.71	34.63	20.96
11.000	5.12	9.70	33.85	21.21
12.000	5.12	9.65	33.13	21.26
13.000	5.13	9.60	32.44	21.32
14.000	5.15	9.57	31.76	21.46
15.000	5.18	9.56	31.15	21.61
16.000	5.20	9.54	30.53	21.74
17.000	5.19	9.45	29.94	21.65
18.000	5.22	9.45	29.37	21.85
19.000	5.22	9.41	28.79	21.89
20.000	5.19	9.28	28.24	21.65
21.000	5.19	9.22	27.69	21.65
22.000	5.23	9.24	27.14	21.90
23.000	5.20	9.16	26.61	21.98
24.000	5.29	9.26	26.09	22.31
26.000	5.30	9.18	25.07	22.38
27.000	5.30	9.13	24.58	22.38
28.000	5.30	9.08	24.10	22.37
29.000	5.31	9.05	23.62	22.43
30.000	5.32	9.02	23.14	22.50
31.000	5.32	8.97	22.65	22.50

Table 13. ΔC_p^{ads} , ΔH^{ads} , ΔG^{ads} , and ΔS^{ads} of Benzene on Graphite at 298.16° K (Concluded)

Π dynes/cm	ΔC_p^{ads} cal/° K-mole	ΔH^{ads} kcal/mole	$-\Delta G^{\text{ads}}$ kcal/mole	$-\Delta S^{\text{ads}}$ cal/° K-mole
32.000	5.31	8.92	22.21	22.47
33.000	5.32	8.88	21.76	22.50
34.000	5.32	8.85	21.30	22.53
35.000	5.32	8.81	20.87	22.54
36.000	5.33	8.77	20.43	22.56
37.000	5.32	8.72	20.01	22.54
38.000	5.32	8.67	19.59	22.52
39.000	5.54	9.06	19.19	23.95
40.000	5.54	9.01	18.79	23.93
41.000	5.54	8.97	18.40	23.93
42.000	5.54	8.93	18.02	23.91
43.000	5.53	8.88	17.66	23.86
44.000	5.53	8.84	17.30	23.83
45.000	5.52	8.78	16.95	23.76
46.000	5.51	8.74	16.62	23.73
47.000	5.51	8.70	16.28	23.72
48.000	5.50	8.65	15.98	23.65
49.000	5.50	8.62	15.68	23.65
50.000	5.49	8.58	15.40	23.61
51.000	5.49	8.55	15.13	23.60
52.000	5.49	8.52	14.89	23.58
53.000	5.49	8.50	14.66	23.58
54.000	5.48	8.46	14.41	23.54

Note: Five isotherms were used in the calculations up to $\Pi = 39.00$, then the 50° C isotherm dropped out. From $\Pi = 39.00$ to $\Pi = 52.00$, four isotherms were used in the calculations where the 30° C isotherm dropped out at $\Pi = 52.00$. Above $\Pi = 54.00$, no calculations were made since the 25° C isotherm did not extend further and all values of ΔG^{ads} at all Π were calculated using this isotherm.

Table 14. ΔC_P^{ads} , ΔH^{ads} , ΔG^{ads} , and ΔS^{ads} of Benzene on Boron Nitride
at 298.16° K

Π dynes/cm	ΔC_P^{ads} cal/° K-mole	ΔH^{ads} kcal/mole	$-\Delta G^{\text{ads}}$ kcal/mole	$-\Delta S^{\text{ads}}$ cal/° K-mole
0.200	(2.37)	(6.76)	(59.88)	(2.58)
0.400	(2.64)	(6.86)	(55.87)	(4.27)
0.600	(2.72)	(6.75)	(53.12)	(4.84)
0.800	3.14	7.36	50.62	7.72
1.000	3.39	7.67	48.77	9.36
1.400	3.78	8.17	45.99	11.97
1.600	3.94	8.37	44.83	13.05
1.800	4.11	8.60	43.75	14.19
2.000	4.23	8.74	42.78	14.98
2.200	4.32	8.84	41.89	15.60
2.400	4.40	8.94	41.09	16.19
2.700	4.47	8.97	40.00	16.66
3.000	4.51	8.95	39.01	16.95
3.500	4.52	8.82	37.61	16.97
4.000	4.58	8.82	36.33	17.38
4.500	4.63	8.80	35.25	17.70
5.000	4.64	8.73	34.27	17.77
5.500	4.64	8.65	33.37	17.81
6.000	4.68	8.64	32.54	18.07
6.500	4.71	8.64	31.78	18.31
7.000	4.75	8.64	31.09	18.56
7.500	4.77	8.63	30.45	18.73
8.000	4.78	8.59	29.85	18.80
8.500	4.83	8.62	29.30	19.80
9.000	4.85	8.61	28.77	19.22
9.500	4.88	8.63	28.27	19.45
10.000	4.90	8.62	27.80	19.57
10.500	4.91	8.59	27.35	19.64
11.000	4.94	8.61	26.92	19.84
11.500	4.96	8.60	26.50	19.97
12.000	4.98	8.60	26.10	20.10
13.000	5.02	8.62	25.31	20.43
14.000	5.07	8.63	24.60	20.71
15.000	5.09	8.60	23.92	20.84
16.000	5.11	8.59	23.27	21.02
17.000	5.15	8.60	22.67	21.24
18.000	5.16	8.57	22.09	21.35
19.000	5.19	8.58	21.54	21.55

Table 14. ΔC_p^{ads} , ΔH^{ads} , ΔG^{ads} , and ΔS^{ads} of Benzene on Boron Nitride
at 298.16° K (Concluded)

Π dynes/cm	ΔC_p^{ads} cal/° K-mole	ΔH^{ads} kcal/mole	$-\Delta G^{\text{ads}}$ kcal/mole	$-\Delta S^{\text{ads}}$ cal/° K-mole
20.000	5.19	8.53	21.00	21.57
21.000	5.20	8.50	20.50	21.64
22.000	5.23	8.50	20.00	21.81
23.000	5.25	8.50	19.54	21.95
24.000	5.26	8.47	19.08	22.01
25.000	5.29	8.49	18.65	22.21
26.000	5.31	8.48	18.22	22.33
27.000	5.32	8.46	17.82	22.41
28.000	5.34	8.46	17.43	22.54
29.000	5.34	8.43	17.08	22.54
30.000	5.35	8.41	16.73	22.60
31.000	5.36	8.40	16.40	22.69
32.000	5.37	8.39	16.07	22.76
33.000	5.37	8.36	15.78	22.76
34.000	5.38	8.35	15.50	22.81
35.000	5.36	8.28	15.23	22.68

All calculations were made using the 30° C, 25° C, 15° C,
and 0° C except above $\Pi = 35.00$, where the 30° C isotherm
was not used.

Table 15. Limits on ΔC_P^{st} and ΔH^{st} for Both Adsorbents
as a Function of the Weight Adsorbed

W_a for Graphite mg/gm	W_a for Boron Nitride mg/gm	ΔC_P^{st} cal/° K-mole	ΔH^{st} kcal/mole
0.10 - 0.50	0.10 - 0.70	± 0.2	± 1000
0.50 - 1.00	0.70 - 1.50	± 0.15	± 750
1.00 - 1.50	1.50 - 2.20	± 0.10	± 500
1.50 - 2.00	2.20 - 3.00	± 0.075	± 300
2.00 - 3.00	3.00 - 5.00	± 0.04	± 150
3.00 - 4.00	5.00 - 10.00	± 0.08	± 100
4.20 - 9.75	10.00 - 13.00	± 0.10	± 150

Limits on ΔC_P^{ads} and ΔH^{ads} are difficult to estimate as the error depends upon values of Π . Since errors introduced in Π at low pressures are also found in Π at high pressures, the errors are additive. It is estimated that Π is known to within ± 0.50 dynes/cm thus making the error in ΔC_P^{ads} and ΔH^{ads} possibly very high at low pressures. It is estimated that the error in:

ΔH^{ads} is ± 500 cal/mole above $\Pi > 2.0$ dynes/cm
 ΔC_P^{ads} is ± 0.2 cal/° K-mole above $\Pi > 2.0$ dynes/cm
 ΔS^{ads} is ± 1.5 e.u. above $\Pi > 2.0$ dynes/cm

CHAPTER IV

CONCLUSIONS

The surface area of the Sterling FT (2700°C) carbon black used for these measurements was $11.7 \pm 0.1 \text{ m}^2$ per gram of sample, determined by the BET method using benzene and CCl_4 as the adsorbates.⁴ The surface areas obtained by Kiselev et al. and Beebe et al. were 12.23 m^2 per gram of sample. If the differences in surface area between our sample and those obtained by the above workers are taken into account, Kiselev's values of W_a , when used in the Clausius-Clapeyron equation in connection with the data of the present work, gave similar values of ΔH^{st} with ΔH^{st} obtained solely from our data. Kiselev's absolute isotherm curve was weighted heavily towards the results obtained from Sterling MT (3100°C) graphitized thermal black! Kiselev's "differential heat of adsorption" values, obtained by use of a calorimeter, were the same as ours within experimental error above one mg of adsorbate per gram of sample.⁹

In another paper, Kiselev gives theoretical means by which the differential entropy of adsorption can be obtained.³ In the limiting case where $\theta = 0.3$, he calculated a value of ΔS^{ads} of 18.6 e.u. at 293.16° K which is close to the value of ΔS^{ads} at 298.16° K obtained here. The agreement at higher values of θ was much better. ΔS^{ads} remains nearly constant over the range of Π from 0 to 36 dynes/cm at a value of $21.5 \text{ e.u.} \pm 1.7 \text{ e.u.}$ This is a strong indication that the molecular movement of benzene on the graphite surface remains approximately the same

up to a coverage of $\theta = 2.5$. It must be remembered that the values of Π are additive so that errors in Π at low pressures will influence Π values at higher pressure. The benzene molecule apparently possesses two degrees of translational freedom and has hindered rotation about the axis lying in the plane of the benzene molecule, but free rotation in the plane of the benzene ring.

It should be noted that ΔH^{ads} at low coverages is quite high but approaches the heat of condensation of benzene at high coverages. A decrease in the values of ΔH^{ads} , ΔS^{ads} , and ΔH^{st} resulted when data from the 50° C isotherm were not used in calculating these thermodynamic quantities. As there was no justification for disregarding the 50° C isotherm, it was used in the calculations. The - 20.8° C isotherm was not used in any of the calculations due to poor temperature bath control.

Isotherms have been attempted using water as the adsorbate and preliminary results indicate that water is chemisorbed. A type II isotherm was obtained with water on boron nitride in contrast to the type III isotherm obtained with water on graphite.¹⁰ Ross, et al. indicated that samples of boron nitride used in previous experiments did have a surface contaminant, possibly boric acid. Also, indications exist that the samples of boron nitride previously used have very homotattic surfaces.

The values of ΔS^{ads} obtained indicate that benzene molecules may possess only slightly hindered rotation on a boron nitride surface as well as two degrees of translational freedom when $\theta < 0.3$. At coverages of $\theta > 1.0$, the same restrictions in molecular motions appear to result with the two adsorbents. However, two-dimensional translation with hin-

dered rotation about the axes lying in the plane of the benzene molecule but having free rotation in the plane of the ring is apparently correct for benzene on boron nitride at $\theta > 1.0$. There is no reason to believe that localization of benzene on boron nitride exists.

Further evidence that, at low coverages ($\theta < 0.3$), benzene is loosely adsorbed by boron nitride relative to the strong adsorption of benzene on graphite is that ΔH^{ads} is less than 8.0 kcal/mole at $\Pi = 2.0$ dynes/cm and lower. This fact, plus a study of ΔS^{ads} values in this region, indicates that a change in the adsorbate-adsorbent or adsorbate-adsorbate interaction energy occurs as more benzene molecules are adsorbed on the surface.

CHAPTER V

RECOMMENDATIONS

By use of the Cahn balance along with newer and more sensitive capacitance manometers than used here, the low pressure portions of the various isotherms can be readily obtained, which will enable the researcher to gain new insights into the physical changes that occur on the surface during physical adsorption. While the data presented in this work are much more accurate than those usually found in physical adsorption works, much better data could be obtained, especially in the pressure measurements. An order of magnitude better pressure measurements could be obtained by using one of the newer capacitance manometers, which can be read to ± 0.0005 Torr, and also by using a more sensitive cathetometer with a mercury (or oil) manometer.

The second major improvement would be the complete elimination of any stopcock grease in the apparatus through the use of high vacuum metal valves. Without the contamination of stopcock grease by most organic vapors, using the Cahn balance-capacitance manometer system kinetic data could be obtained even in the rapid process of physical adsorption. Kinetic data for so rapid a process may be of considerable importance. The time for equilibrium to be established in the system is on the order of ten minutes for benzene on both adsorbents at low pressures, becoming almost instantaneous at coverages of around one monolayer, then again becoming even slower than the rates at low coverages as coverages above two

monolayers are reached.

As boron nitride is being used more and more in basic research of physical adsorption, a study of treatment given to a boron nitride sample is certainly in order. The problem of water adsorption shows that some vast differences do exist and in any comparison of the two adsorbents, one should take this into account. The comparison of two different samples of boron nitride may be possible by benzene adsorption, although a line of research comparable to that of Kiselev's work on the graphitized thermal blacks would be necessary to achieve this.

Through the use of a microbalance-capacitance manometer system with the above suggested modifications, very reliable and accurate isotherms can be obtained very quickly. For instance, three isotherms of an adsorbate-adsorbent system with two runs of about fifty data points each can be obtained in six, eight-hour days with weight increases measured to an absolute accuracy of ± 0.01 mg/gram of sample and pressure measurements of less than 0.1 percent error in absolute pressure data over the entire range of measured data.

LITERATURE CITED^{*}

1. Isirikyan, A. A. and Kiselev, A. V., J. Phys. Chem., 65, 601 (1961).
2. Davis, Bruce W., "Adsorption on a Graphitized Carbon Surface," Ph.D. Thesis, University of California, Riverside, Calif., June, 1964.
3. Kiselev, A. V. and Poshkus, D. P., Trans. Faraday Soc., 59, 428 (1963).
4. Brunaur, S., Emmett, P. H., and Teller, E., J. Am. Chem. Soc., 60, 309 (1938).
5. Barr, W. E. and Anhorn, V. J., Scientific and Industrial Glass Blowing and Laboratory Techniques, Instruments Publ. Co., Pittsburgh, 1949.
6. Dushman, S., Scientific Foundation of Vacuum Technique, J. M. Lafferty, ed., second edition, Wiley, New York, 1962.
7. Ross, S. and Olivier, J. P., On Physical Adsorption, Interscience Publishers, New York, 1964.
8. Schaeffer, W. D., Smith, W. R., and Polley, M. H., Ind. Eng. Chem., 45, 1721 (1953).
9. Kiselev, A. V. and Lygin, V. I., Kolloidn. Zh. (English translation), 23, 478 (1961).
10. Young D. M. and Crowell, A. D., Physical Adsorption of Gases, Butterworths, Washington, 1962.
11. Instruction Manual for the Cahn RG Automatic Electrobalance, Cahn Instrument Co., Paramout, Calif.
12. Hill, T. L., Emmett, P. H., and Joyners, L. G., J. Am. Chem. Soc., 73, 5102 (1951).
13. American Petroleum Institute Research Project 44, Table 21K (Part 1), Carnegie Institute of Technology, Pittsburgh, Pa., April 30, 1954.

^{*} Abbreviations used herein follow the form found in Chemical Abstracts, 55 (1961).

LITERATURE CITED (Concluded)

14. Sams, J. R., Constabaris, G., and Halsey, G. D., J. Phys. Chem., 66, 2154 (1962).
15. Prenzlowl, C. F. and Halsey, G. D., J. Phys. Chem., 61, 1158 (1957).